Electrothermal Actuators with Ultrafast Response Speed and Large Deformation

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The ability to fabricate electrothermal actuators (ETAs) simultaneously featuring ultrafast response speed (within 0.1 s), large deformation (bending for at least 360°), high figure-of-merit (FoM, larger than 0.1%), and low driving voltage (smaller than 1 V) in a single device is extremely important and challenging for their applications in artificial muscles, switches, and microsensors for robotics and biomimetic devices. Herein, an ETA composed of a silver nanowire (AgNW) layer and an ultrathin linear low-density polyethylene (LLDPE) film with all the aforementioned features is designed. Due to the high conductivity of the AgNW layer and the great difference between the coefficients of thermal expansion of AgNW layer and LLDPE film as well as the huge change in the heat transfer coefficient between flat and rolled ETA, the obtained ETA exhibits an ultrafast response speed of 0.08 s for a bending angle of 360° with a FoM of 0.46% at a low driving voltage of 1 V, over one order of magnitude larger than those of reported ETAs. As a proof-of-concept application, the as-prepared ETAs can be used as intelligent mechanical devices with excellent performance.

1. Introduction

With the rapid development of robotics and biomimetic intelligent devices, demand for high-performance soft actuators has been increasing.1–3 Soft actuators can be driven by a variety of external inputs. Among these, electricity is the most readily available source for industrial standardization. Electroactive polymeric (EAP) actuator is one of the most explored actuators driven by electricity and has the advantage of fast response and large deformation.4–6 Alternatively, electrothermal actuator (ETA) is another type of electricity-driven actuator that obviates the use of high operating voltage and electrolyte.7–19 The fundamental principle of ETA is leveraging the thermal expansion gradient with electricity input. Specifically, for a bimorph ETA consisting of two layers with vastly different coefficients of thermal expansion (CTE), the device will bend to the side with the lower CTE when it is heated up. It is generally accepted that ETAs possess advantages, including but not limited to, large generated strain, low driving voltage, ease of fabrication, and electrolyte free.

High-performance ETAs are generally characterized by fast response speed at low driving voltages, large deformation, and high figure-of-merit (FoM).20 Unfortunately, until now, the response rate of soft ETAs falls in the range of 1–40° s⁻¹ (Table S3, Supporting Information). Dielectric elastomer actuators can respond in milliseconds; yet the driving voltage is as large as 1 kV.21 A VO₂-based phase-change ETA can achieve a response frequency of 100 Hz. However, the deformation is limited to submillimeter scale.22 In addition, deformation of ETAs reported in the literature is typically smaller than 360° or the radius of curvature is lower than 3 cm (Table S3, Supporting Information). An ETA that simultaneously has response speed and deformation comparable to those of EAP is still elusive. The driving voltage of ETAs is usually as high as tens of volts, and the FoM is however below 0.1%, similar to actuators driven by photo energy, moisture, and electricity (Table S3, Supporting Information).

With respect to the ETA, the external input of a driving voltage is required to convert electrical energy to thermal energy. Therefore, a conductive electrode is needed to function as a heater. For a bimorph-structured ETA, a conductive layer with a low CTE could be combined with another layer with a high CTE. Conductive materials such as carbon nanotubes, graphene, silver nanowires (AgNWs), and organic conductors have been used as electrodes.23–25 Among these materials, carbon nanotubes and graphene have negative CTEs which are conducive to a large deformation.23,24 However, carbon material heaters usually show an inferior electrical conductivity (under 1000 S cm⁻¹).15 Therefore, it is not possible to achieve a large deformation at a relatively low driving voltage. AgNWs have also been used as heating electrodes for the ETA. However, the electrical conductivity of AgNW films remains below 6000 S cm⁻¹, which is insufficient to obtain highly conductive heating electrodes.26 It is arguable that the resistance of the heating electrode can be reduced by increasing the thickness of the conductive material (for example, carbon materials and AgNWs). An increase in...
thickness unfortunately has a negative effect on the response time and the deformation. Consequently, conducting materials with an electrical conductivity higher than 10 000 S cm\(^{-1}\) at a thickness smaller than 1 μm to achieve a large deformation (larger than 360° or 3 cm\(^{-1}\)) at a driving voltage of 1–2 V are desired if the difference in the CTEs is large enough for the bimorph structure.\(^{[27]}\) Therefore, LLDPE is a promising candidate used as the bending layer for bimorph-structured ETAs due to its large CTE difference when compared with AgNW heat layer (\(\alpha_{\text{LLDPE}} = 502.7 \times 10^{-6} \text{ K}^{-1}\) vs. \(\alpha_{\text{AgNWs-HPMC}} = 5.4 \times 10^{-6} \text{ K}^{-1}\), Table S2, Supporting Information). More importantly, the minimum thickness of the bimorph structure is also a prerequisite for obtaining a microsecond time-scale response.

In principle, it is necessary to optimize the combination of the bimorph structure to achieve a large deformation and fast response speed at a certain driving voltage. A valid approach is to adjust the heat transfer coefficient (HTC) of the bimorph structure.\(^{[27–29]}\) Theoretically, the value of HTC is positive to response speed and negative to deformation, respectively (See Equation 1–3, Supporting Information). Ultrafast response speed and ultralarge deformation cannot coexist if the value of HTC remains the same during the whole bending process.\(^{[14–19]}\) Therefore, ETAs that simultaneously exhibit fast response speed (within 0.1 s) and large deformation (bending for at least 360°) in a single device has never been achieved.\(^{[17]}\) For a bimorph-structured ETA, ideally, at the initial stage of deformation, the value of HTC of the ETA should be low enough to achieve fast response speed; whereas at the end of the deformation, the value of HTC of the ETA should be high enough to achieve large deformation. This requirement imposes stringent restrictions on the selection of suitable materials for assembling the bimorph structure.

Herein, we show that by combining a highly conductive AgNW layer (having an electrical conductivity greater than 25 000 S cm\(^{-1}\)), formed by an interpenetrating network of AgNWs with large and small diameters (150 nm vs. 22 nm) with a thin linear low-density polyethylene (LLDPE) with a large CTE (\(\alpha_{\text{LLDPE}} = 502.7 \times 10^{-6} \text{ K}^{-1}\)), an ETA with an ultrafast response speed (0.08 s for 360°, or tip movement speed of 12.5 cm s\(^{-1}\)) and a large deformation (curvature 8.8 cm\(^{-1}\)) can be achieved under a low driving voltage (1–2 V). We attribute this high performance of our ETA to the highly conductive AgNW layer and immense difference in CTEs between AgNW layer and LLDPE film as well as the huge change in the HTC between flat and rolled ETA. More interestingly, the ETA can roll continuously to a small radius. The FoM of the ETA in this work is as high as 0.46%, and it is demonstrated that the ETA can sustain more than 1000 folds of its own weight.

2. Results and Discussion

Figure 1 schematically illustrates the fabrication process of AgNWs/LLDPE bimorph ETA. First, AgNWs with two different average diameters (150 and 22 nm) were synthesized by a modified polyl reduction route\(^{[30,31]}\) and purified via dynamic agitation-induced centrifugal purification.\(^{[32]}\) Afterward, a certain amount of hydroxypropyl methyl cellulose (HPMC) was added to the mixed AgNW ink (with a desired ratio of thick and thin AgNWs) to improve the adhesion of AgNWs to substrates.\(^{[33]}\) Then, a mixed AgNW film was fabricated using the prepared ink through the Mayer rod coating method on the UV–Ozone pretreated LLDPE layer on an organic glass substrate. Afterward, the compact AgNWs/LLDPE film was peeled off from the substrate and connected with copper wires by conductive silver paste. At last, the ETA could successfully function with input voltage (See details in Experimental Section).

For a bimorph ETA with a small aspect ratio (0.8 cm × 0.5 cm × 9.5 μm, Figure S1, Supporting Information), it can roll for one cycle within 0.08 s under a driving voltage of 1 V, and continuously roll further to a smaller radius for a second cycle within 0.52 s (Figure 2 and video 1, Supporting Information). The tip movement speed corresponds to 12.5 cm s\(^{-1}\), larger than a graphene–organic bimorph actuator which showed a tip movement speed of 50 μm s\(^{-1}\).\(^{[34]}\) The response speed is one order of magnitude faster than that of the best reported ETAs in the literature (Table S3, Supporting Information). To explore the full potential of the ETA for shape deformation, an ETA with a larger aspect ratio (5 cm × 1 cm × 9.5 μm, Figure S1, Supporting Information) was fabricated. This device can continuously roll for six cycles under a low driving voltage of 2 V (Figure 2b and

![Figure 1. Schematic illustration of the fabrication process of AgNWs/LLDPE bimorph ETA.](image-url)
The temperature and the curvature change along with the rolling of the ETA are shown in Figure 2c, where the variation of the temperature and the curvature follow the same trend. At around 7 s, both the temperature and the curvature reach the highest value. The ETA can roll up and straighten repeatedly (Figure 2d). After 500 cycles, the curvature still keeps stable (Figure 2e). Curvatures calculated from Equation 1 (See details in Supporting Information) and measured experimentally were compared in Figure S2, Supporting Information. The theoretical results fitted well with the experimental data among the small temperature change (less than 20 °C). When the temperature change was larger than 20 °C, experimental data deviated positively from theoretical results, which might originate from gentle softening of LLDPE.

The response time and the deformation of different ETAs under a certain driving voltage were compared in Figure 3. Our ETA exhibits the fastest response speed and the largest deformation under the lowest driving voltage. Furthermore, as shown in Figure 3b,c, the performance of actuators driven by photoenergy, moisture, as well as electric energy was also evaluated.
for comparison. The actuators driven by moisture can achieve a larger deformation but with a longer response time compared with our ETA (Figure 3b). In addition, our ETA also surpasses all other actuators from the perspective of FoM (Figure 3c), which goes up to 0.46%, three times higher than that of the best actuator (0.1%) as reported in the literature (See details in Supporting Information).[17]

It is noteworthy that the mixed AgNW film exhibits a sheet resistance of 0.6 Ω sq⁻¹ with a minimal thickness of 0.6 μm (Figure S1c, Supporting Information), which reveals a high electrical conductivity of 27 000 S cm⁻¹. However, to achieve the same sheet resistance, the thickness of the film fabricated with pure AgNWs with diameters of 150 or 22 nm is 4.1 or 1.0 μm (Figure S3a,b, Supporting Information). Furthermore, the AgNWs in the mixed film are much sparser than those in pure films, fitting well with the thickness (Figure S4a–c), Supporting Information. Compared with the pure AgNW films, the mixed AgNW film exhibits better electrical conductivity and enhanced optical performance. It is possible that thick AgNWs form the network, and thin AgNWs bridge adjacent thick AgNWs and reduce the resistance of the network (Figure S4d, Supporting Information). This phenomenon is quite similar to the dual-scale metal nanowire network transparent conductor for highly efficient and flexible organic light-emitting diodes reported previously.[35]

It is particularly interesting that at the same driving voltage, the flat ETA heated to a much lower temperature than the rolled ETA. The rolled ETA can heat up to 53.8 °C at 2 V, whereas the flat ETA can heat up to the same temperature at a voltage larger than 6 V (Figure 4 and Figure S5, Supporting Information). The dependence of the temperature rise on the input power density is shown in Figure 4b. Similarly, the rolled ETA heats up at a much lower power input compared with the flat ETA. The HTC of the rolled and flat ETAs can be calculated from Figure 4b. What inconceivable is, the HTC of the flat ETA is 336.1 W K⁻¹ m⁻², more than an order of magnitude larger than that of the rolled ETA (14.8 W K⁻¹ m⁻²). The great change in the HTC between flat ETA and rolled ETA has never been reported before. The reason for this phenomenon could be the nature of the LLDPE itself, which requires further investigation. We deem that the great difference in the HTC is the key factor that simultaneously affects the response speed and the deformation of our ETA.

The ETA not only responds unprecedentedly fast and achieves extremely large deformation under a low driving voltage but also converts electrical energy to mechanical energy efficiently. An ETA with a mass of 6.0 mg can hold an object with a mass of 10 g, which is more than three orders of magnitude larger than that of the ETA itself (Figure 5 and video 3, Supporting Information). The ETA can also lift up an object in a dynamic process, achieving an energy-to-mass ratio.

Figure 3. Comparison of the actuating performance of our ETA with the literature reported ETAs. a) Response time and curvature versus driving voltage. b) Curvature versus response time. c) Energy efficiency versus response time.
of 1.6 J kg$^{-1}$ (Figure 5b and video 4, Supporting Information). The output force generated by the ETA was measured as vertical blocking force shown in Figure 5c. The force increased with the input power density, and can reach 0.32 mN at an input power density of 0.045 W cm$^{-2}$ for a 9.5 $\mu$m-thick ETA. This input power density corresponds roughly to a temperature rise of 10°C according to Figure 4b, compared favorably to the force output by a metallic actuator (0.02 mN for a temperature rise of 10°C)$^{[16]}$. More interestingly, as shown in Figure 5d, it is found that when a block of polyester foam (thermal conductivity 0.02–0.04 W m$^{-1}$ K$^{-1}$) was placed in a hand wearing a nitrile glove, even the temperature difference between the foam and the environment (25°C) can drive the rolling up of the ETA (video 5, Supporting Information), demonstrating the extremely high temperature sensitivity of the ETA.

3. Conclusion

In summary, AgNWs/LLDPE bimorph ETAs have been fabricated in this work. The actuators meet the four key performance metrics of actuators, and simultaneously exhibit an ultrafast response speed of 0.08 s for a bending angle of 360° with a FoM of 0.46% at a low driving voltage of 1 V. All these
performance metrics are the best for ETAs, and among the best for all types of actuators. The key to the striking performance lies in the high electrical conductivity of AgNW film of the inter-penetrating structure of two different diameters, an ultrathin LLDPE film of enormous coefficient of thermal expansion and great change in the HTC between flat and rolled ETAs. This promising bimorph ETA will find significant applications as high-performance artificial muscles in biomimetic devices and robotics.

4. Experimental Section

Materials: AgNO₃, NaCl, NaBr, ethylene glycol (EG), and ethanol (ET) were obtained from Sinopharm Chemical Reagent Co. Ltd. CuCl₂ was purchased from Shanghai Tian Titan Scientific Co. Ltd. HPMC was received from Aladdin. Poly(vinylpyrrolidone) (PVP, K90) were received from Sigma-Aldrich. All chemicals were analytical reagents and used without further purification. DI water (18.2 MΩ cm) was produced using an ultrapure water system (GBW-1). LLDPE was received from Jindun Packaging Co. Ltd. Organic glass was purchased from Huayou Acrylic Processing Co. Ltd.

Preparation of Thick AgNWs: Thick AgNWs (about 150 nm in diameter) were synthesized according to the literature with minor modifications. In a typical synthesis, fresh AgNO₃ (0.9 g) was added into 20 mL of EG and mixed under ultrasonication at 4–8 °C until a complete dissolution was reached (5–6 min). CuCl₂·2H₂O (0.0132 g) was dissolved in 16 mL of EG. PVP (K90, 0.421 g) and PVP (K90, 0.406 g) were dissolved in EG (115 mL), and heated at 130 °C for 25 min to reach complete dissolution, and then heated to 140 °C in a 250 mL flask in an oil bath. Subsequently, 3.2 mL CuCl₂ solution and 20 mL AgNO₃ solution were added dropwise into PVP solution within 5 min. The reaction was held for 50 min. After completion of the reaction, the flask was removed from the oil bath and the solution was quenched to room temperature.

Synthesis of Thin AgNWs: Thin AgNWs (about 20 nm in diameter) were synthesized by polyol reduction methods. In a typical synthesis, (A) 220.0 mM NaBr, (B) 210.0 mM NaCl, and (C) 505.0 mM PVP K90 in EG were prepared at first. EG (116 mL) solution A (1 mL), solution B (2 mL), solution C (15 mL), and fresh AgNO₃ (0.6765 g in 15 mL of EG) were mixed under ultrasonication at 4 °C, and then heated sequentially into a 250 mL flask which was placed in an oil bath at room temperature. Then the solution was stirred mechanically at 300 rpm min⁻¹ for 30 min. After stirring, the temperature of the oil bath was slowly increased to 180 °C in 20–25 min. Meanwhile, during the heating process, nitrogen gas (150 mL min⁻¹) was introduced into the solution. When the temperature reached 180 °C, nitrogen gas was shut off and the temperature of the oil bath was set to 170°C. After 10 min, stirring was stopped and the reaction was held for 1 h without disturbance. After completion of the reaction, the flask was removed from the oil bath and the solution was cooled in water to room temperature.

Purification of AgNWs: Thick AgNWs and thin AgNWs were all purified by dynamic agitation-induced centrifugal purification. The as-prepared AgNW mixture was mixed with DI water and then poured into the filtration membrane-based cylinder chamber with pores (8 μm); the stirring speed of the mechanical agitator was set at 900 rpm, with six-holes stirred oar stirring paddles. DI water flowed continuously into the filtration setup to compensate for the filtrate solution being removed and to maintain a stable concentration AgNWs in the feed solution. After purification for varying times (60 min), the continuous addition of DI water was stopped, while the stirring and washing-off continued to concentrate the solution to the desired AgNW concentration. The purified AgNWs were collected from the bottom of the filtration membrane-based cylinder chamber.

Preparation of AgNWs/LLDPE Bimorph: For the preparation of AgNWs/LLDPE bimorph, with a desired ratio of thick AgNWs and thin AgNWs (mass ratio 12:1), a certain amount of HPMC aqueous solution (2 mg mL⁻¹) was used to improve the adhesion of AgNWs to substrate, so the ink containing AgNWs (2.1 mg mL⁻¹) was prepared. LLDPE was covered on organic glass and then treated with ultraviolet–ozone for 10 min. Mixed AgNW film was fabricated on LLDPE substrate using an automatic coating machine at a coating speed of 120 mm s⁻¹. The coated films were dried in the atmosphere at 60 °C for 5 min. The AgNWs/LLDPE film was peeled off from the substrate and cut into the desired shapes and dimensions. Cu wires were attached to the two ends of the heaters by silver-conducting paste for connection to the power supply.

Characterization: The morphology of the ETA and the thickness of films (d) were characterized by scanning electron microscopy (SEM) (Nova NanoSEM 450). The sheet resistance (Rₛ) of ETA was measured using a four-point probe method (RST-9), and the electrical conductivity of films was calculated by σ = Rₛ×t⁻¹. The voltage was supplied to the heaters by a power supply (IT6831B) and the resulting bending angles of the bimorph actuator were recorded using a digital camera. The temperatures of the AgNWs/LLDPE heaters and the bimorph actuators were measured in real time using a contact infrared camera (C300) placed right over the heaters or actuators. The resistance of AgNWs/LLDPE bimorph actuators was measured using a Keithley 2450 SourceMeter. Note that the response time is also affected by environment temperature, especially for thin film. In this work, the environment temperature was kept at ≈25°C to minimize the influence of environment temperature. On the other hand, the actuation force is sacrificed to some extent to maximize the response speed because of the thin-film layer used.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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