Multistimuli-Responsive Insect-Scale Soft Robotics Based on Anisotropic Super-Aligned VO₂ Nanowire/Carbon Nanotube Bimorph Actuators

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The emerging soft robots have attracted increasing interests and gotten rapidly developed, but it is still challenging to substantially promote their response speed and work density. In addition, the wireless way to conveniently trigger the devices, especially for the centimeter-scale ones, is highly desired. Herein, the multistimuli-responsive insect-scale soft robotics is reported based on a super-aligned VO₂ nanowire arrays (NAs)/carbon nanotube (CNT) bimorph film, comprehensively addressing aforementioned problems. The as-prepared VO₂ NA/CNT bimorph shows improved actuation performance, anisotropic behavior, rapid response to various stimuli (heat, light, and electricity), and multiple movement modes (bending and torsion). Consequently, diverse untethered, insect-scale soft robots, serving as biomimetic crawler, lifter, gripper, wing of flying robots, torsional robot, and so on are successfully demonstrated. The findings provide an effective strategy to develop high-performance macroscopic mechanical devices by assembling functional nanostructures.

1. Introduction

Microrobotics, one of the latest techs in the 21st century, enables the fine manipulation of mechanical behavior such as locomotion and operation at a small scale. Taking advantage of small physical size and finite inertial forces, microrobots are usually tasked with searching, infrastructure inspection, and equipment maintenance within confined environments. Therefore, flexible robots in insect-scale are highly desired owing to their good adaptation to the aforementioned specific application scenarios. Accordingly, the further development of ideal millimeter-to-centimeter actuators, with high work density, large displacement, rapid response, superior flexibility, good stability, and multiple stimuli, necessitated intensive studies on advanced driving mechanisms and high-performance actuation materials.

Recent advances have developed conventional macrorobots to miniaturized insect-scale robots driven by piezoelectric ceramics or shape-memory alloys (SMAs), such as crawling robots,[1-3] climbing robots,[4] and even untethered flight vehicles.[5] Despite remarkable actuation performances, these devices contain relatively rigid components that limit their colossal shape changes and required flexibility. By contrast, soft robots that are based on organic matters or carbon nanotube (CNT) structures can sensitively respond to temperature,[6,7] light,[8,9] electricity,[10,11] magnetism,[12] humidity,[13,14] and so on. They can demonstrate good flexibility and response to external perturbations, but most of them suffer from slow response speeds, and rely on specific conditions that are rarely accessible such as magnetic fields or ultrahigh voltages. Therefore, there is a serious challenge to build up flexible and versatile insect-scale robots, which could rapidly respond to multiple stimuli and function under easily accessible and operable driving conditions, in particular wirelessly powered mode.

Vanadium dioxide (VO₂), emerged as an ideal actuator material in recent years, has the potential to address all the challenges to develop insect-scale untethered robots with supreme performance. VO₂ has a unique reversible metal–insulator transition (MIT) at T ≈ 341 K (close to room temperature), accompanied with a large strain of ≈1% along the c-axis of its high-temperature rutile phase (cₐ-axis).[15,16] With an outstanding elasticity, VO₂ has a superior theoretical work density of 7 J cm⁻³,[17] higher than most of the existing actuator materials. As reported in reported works, the abrupt strain change of single-crystalline VO₂ nanobeam-based bimorph actuators not only enables a large

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amplitude (amplitude/length ratio \(\approx 1\)), but it also promises a high work speed at the order of kilohertz.\[17-21\] In addition, the good structural and chemical stability of the crystalline inorganic oxide guarantees a quite long lifetime for VO\(_2\)-based devices.

Various advanced mechanical devices with sizes ranging from tens of microns to millimeters, such as mechanical claws,\[22\] torsional micromuscles,\[23\] micromechanical optical modulators,\[24\] efficient micromechanical resonators,\[25\] and so on, have been fabricated using this amazing material (VO\(_2\)); they have demonstrated outstanding performances driven by various external stimuli, including heat, light, and electricity. However, owing to the fact that the colossal strain change of VO\(_2\) can only carry out along \(c_f\)-axis, the strain of randomly oriented VO\(_2\) domains in polycrystalline thin film is mainly canceled out. As a result, most of the polycrystalline VO\(_2\) films, which can be potentially applicable for insect-scale devices, can only generate a small strain of \(\approx 0.3\%\) with a corresponding low work density of 0.63 J cm\(^{-3}\).\[17\] Therefore, effectively utilizing the superiority of VO\(_2\) in insect-scale soft robotic devices remains as a key challenge as per the insurmountable obstacles for direct fabrication of highly oriented VO\(_2\) films and oriented VO\(_2\) nanostructures in large scale.

In this work, we develop an insect-scale robotic platform actuator based on super-aligned VO\(_2\) nanowire array (NA)/CNT bimorph with several key advancements: 1) a two-step strategy is developed to fabricate centimeter-scale super-aligned VO\(_2\) NA films to reach a large strain of \(\approx 0.614\%\) along the longitudinal direction, close to that of single-crystalline ones; 2) the introduced VO\(_2\) NA/CNT bimorph demonstrates a comparable actuation performance with those that are based on single-crystalline VO\(_2\), including a giant displacement/length (\(D/L\)) ratio of 0.83, high work density of 2.64 J cm\(^{-3}\), fast response of \(\approx 15\) Hz, and long lifetime of more than 1 000 000 actuation cycles; 3) due to the good electrical conductivity and efficient optical absorption of CNT, the actuator can sensitively respond to multiple external stimuli, i.e., heat, electricity, and light, so as to be wirelessly driven; 4) the bimorph characteristic depicts cutting direction-dependent bending morphologies and actuation performance, enabling multiple functions of the insect-scale mechanical device for extensive applications, especially biomimetic applications, including soft crawlers, powerful lifters, wings of flying robots, clam, and so on.

2. Results and Discussion

The preparation process of VO\(_2\) NA/CNT bimorph uses the steps in Figure 1a. First, ultra-long H\(_2\)V\(_3\)O\(_8\) nanowires (NWs) with the length of hundreds of micrometers and the diameter of hundreds of nanometers were synthesized in a large quantity by a hydrothermal process (see details in Section 4 and Section S1, Supporting Information). Super-aligned H\(_2\)V\(_3\)O\(_8\) NA film was prepared by a facile self-assembly strategy (see details in Section 4 and Section S2, Supporting Information).\[26\] In brief, H\(_2\)V\(_3\)O\(_8\) NWs were uniformly dispersed in a three-phase system that consisted of air phase, water phase (ethanol and water), and oil phase (chloroform) at an appropriate ratio. Driven by the pressure difference between the oil–water interface and air–water interface, the NWs climbed up to water–air interface assembled in parallel to the container sides due to surface tension and capillary force; consequently, the self-alignment of H\(_2\)V\(_3\)O\(_8\) NWs was achieved within the air–water interface and oil–water interface (Figure 1b and Figure S3, Supporting Information). The H\(_2\)V\(_3\)O\(_8\) NA films at the upper and lower interfaces of the water layer were evidently seen in Figure 1b, where the 5 cm-side length of the quartz container determines the maximum centimeter scale of the as-fabricated NA films. In Figure 1c, the as-obtained H\(_2\)V\(_3\)O\(_8\) NWs well arranged along one certain direction with a deviation less than \(\pm 2\)°, confirming the excellent assembly feature (an enlarged scanning electron microscope [SEM] image is shown in Figure 1c for a better view).

The as-obtained super-aligned H\(_2\)V\(_3\)O\(_8\) NA film was then stacked with the CNT film, followed by a postannealing treatment at 500 °C for 20 min under a low gas pressure (∼300 Pa), to fabricate the VO\(_2\) NA/CNT bimorph. During the heating process at an oxygen-deficient condition, the H\(_2\)V\(_3\)O\(_8\) NWs were completely converted to VO\(_2\) (M1) phase via a simple deoxygenation reaction. The crystal structure and chemical composition of the annealed product were identified by X-ray diffraction (XRD) analysis and Raman spectroscopy. The diffraction peaks of as-obtained VO\(_2\) NA film in Figure 1d were consistent with JCPDS card no. 43-1051, verifying its almost pure M1 structure at room temperature. The characteristic Raman modes of M1 phase at 140, 192, 223, 308, 390, and 615 cm\(^{-1}\) were also detected in the as-prepared VO\(_2\) NA film (Figure 1e). The SEM and transmission electron microscope (TEM) images (Figure S4, Supporting Information and Figure 1f) confirmed that the annealed product retained the NW-like morphology as pristine H\(_2\)V\(_3\)O\(_8\) NWs and no obvious defects or cracks were observed.

Again, high-resolution transmission electron microscope (HRTEM) image in Figure 1g identified the annealed NW as VO\(_2\) (M1) with good crystallinity. Moreover, the longitudinal direction of the NW was almost consistent with the \(c_f\)-axis equivalent to the [100]M1 direction of VO\(_2\) (M1). We found that the H\(_2\)V\(_3\)O\(_8\) NWs did not perfectly convert to unidirectional single-crystalline VO\(_2\) (M1) NWs due to the lattice mismatch between the two vanadium compounds. As a result, the obtained VO\(_2\) (M1) NW is usually composed of several domains with roughly consistent crystal directions with the \(c_f\)-axis (deviation < \(\pm 15\)°). Thus, the annealed NW was expected to generate strain as large as the single-crystalline NW. This assumption was verified by the optical images in Figure 1h, where a single-annealed NW underwent a complete MIT accompanied with a distinct color change and a colossal strain of \(\approx 1\%\) along the axial direction. This finding provided a strong support to the applications and outstanding performance of as-prepared super-aligned VO\(_2\) NA film in mechanical devices like the other well-developed VO\(_2\) bimorph actuators. Figure 1i shows the cross-sectional view of the bimorph structure with a thickness ratio of 35 μm (VO\(_2\)) to 25 μm (CNT), showing good alignment of VO\(_2\) NA film and fine contact between the two films (refer to Section S4, Supporting Information, for the discussion about the thickness design of the device). In reality, the thickness of VO\(_2\) NA film is usually set as \(\approx 70\) μm and the total thickness of device can reach to 0.1 mm for the optimal performance.

Upon heating, large compressive strain of VO\(_2\) NA film along the longitudinal direction creates the actuating force in VO\(_2\).
NA/CNT bimorph. As shown in Figure 2a, the whole device is initially set as the straight state above the phase transition temperature \(T_c\) as per the annealing temperature of \(> T_c\) for VO\(_2\) bimorphs. When the temperature is gradually reduced to room temperature, each VO\(_2\) NW undergoes a large tensile strain (\(<1\%\)) along the \(c\) axis (Figure 1h). The super-alignment of VO\(_2\) NA film helps to accumulate the strain from each NW and, thus, maximizes the total strain along the aligned direction of NA film across the MIT, which is expected to be as large as 1%.

Owing to the negligible thermal deformation (\(<1 \times 10^{-5}\)\(^{27}\)) of CNT film during the cooling stage, the bimorph device bends toward the supporting layer (CNT film) originated from the axial elongation of VO\(_2\) NWs. To examine the performance limit of this device, a cantilevered belt was cropped from as-obtained VO\(_2\) NA/CNT bimorph along the axial direction of the VO\(_2\) NA film. The temperature-dependent actuation of device shown in Figure 2b reflects a typical hysteresis loop (window width of \(\approx 15^\circ\)C) at \(\approx 65^\circ\)C, that is commonly observed in other VO\(_2\)-based devices\(^{[28,29]}\) matches well with the DSC curves of annealed VO\(_2\) NWs (Section S5, Supporting Information). This featured loop and characteristic working temperature range verify that the driving mechanism of the actuator is the MIT of VO\(_2\) rather than the thermal expansion mismatch between VO\(_2\) and CNT films. Notably, such a 16 mm-long actuator (as shown in Figure 2c), with length:width:thickness = 16:5:0.1 mm, has a vast tip displacement of \(\approx 13.3\) mm, supply- ing a remarkable \(D/L\) of \(\approx 0.83\). Liu et al.\(^{[17]}\) fabricated bimorph actuators based on high quality-oriented VO\(_2\) thin film using pulse laser deposition method and concluded that these devices could demonstrate superior \(D/L\) exceeding 0.9 at the scale of tens of micrometers in contrast to many other actuators, e.g., SMA (\(\approx 0.2\)), polymer (\(\approx 0.4\)), and piezoelectric actuators (\(\approx 0.05\)). It is obvious that the insect-scale VO\(_2\) actuator in this work performs similar to the optimized VO\(_2\)-based microactuators, much better than other kinds of actuators for this purpose.

**Figure 1.** Preparation and characterizations of the synthesized VO\(_2\) NA/CNT actuator. a) Schematic of fabrication processes of synthesizing VO\(_2\) NA/CNT actuator. b) Optical image of self-aligned H\(_2\)V\(_3\)O\(_8\) NW film prepared by the water–oil–air method. Dash semicircles are used to point out the positions of interfaces and edges of NA films. The black arrow indicates the upper H\(_2\)V\(_3\)O\(_8\) NA film distributed within the air–water interface, and the white arrow shows the film within the water–oil interface. c) False color SEM image of the as-prepared VO\(_2\) NA film (scale bar, 10 \(\mu\)m). Inset shows a magnified view of the SEM image after the annealing treatment (scale bar, 2 \(\mu\)m). d) XRD pattern and e) Raman spectrum of the as-prepared VO\(_2\) (M1) NW film after the annealing treatment. f) TEM image of VO\(_2\) NWs (scale bar, 100 nm). g) HRTEM image of a single VO\(_2\) NW (scale bar, 2 nm). The inset figure indicates that the growth direction of the NW is almost consistent with the [100]\(_{M1}\) direction. h) Optical images of the MIT process of a single VO\(_2\) NW accompanied with a length shrink by \(\approx 1\%\) and the typical color change from bright yellow to dark green (scale bar, 10 \(\mu\)m). i) False color SEM image of the side view of VO\(_2\) NA/CNT bimorph on a flatten SiO\(_2\) substrate (scale bar, 20 \(\mu\)m). The inset shows the optical image of centimeter-long VO\(_2\) NA/CNT device.
Compared with the heat-driven mode in VO$_2$ NA/CNT actuator as demonstrated earlier, photothermal actuators driven by light irradiation and electrothermal actuators driven by Joule heat are more desirable in specialized applications due to their capabilities of undergoing wireless or fast control. A CNT film with strong light absorption, good electrical and thermal conductivity, and extremely small heat capacity per unit area enables VO$_2$ NA/CNT actuators to sensitively respond to multiple stimuli (heat–electricity–light). A laser beam with an appropriate power density ($\approx$6000 mW cm$^{-2}$) was used to activate the actuator (see Figure 2d). The photothermal actuator, with the $D/L$ ratio of $\approx$0.5 and good reversibility, showed that the heating effect of applied laser beam is quite efficient and harmless to the structure. Figure 2e shows a U-shape belt actuator in series with an alternative current (AC) power source where an applied bias of 7 V was measured to completely drive the actuation of device. The relatively large $D/L$ of $\approx$0.75 indicates that the uniform heating from electricity can work more efficiently to drive the actuator than the local heating of laser beam. Despite the large size, the energy consumption of this kind of device is still comparable with the reported microscale VO$_2$ actuators ($800–2.9 \times 10^4$ mW cm$^{-2}$), offering its great potential for energy-saving applications. In addition, the relatively high $T_c$ of VO$_2$ causes an extra energy cost for the temperature increase by $\approx$40 °C. The well-developed MIT modulation techniques of VO$_2$ have been proved to effectively lower its $T_c$ to near room temperature$^{[22,31,32]}$ and thus the power required for this device can be dramatically decreased.

To measure the ultimate response speed of the VO$_2$ NA/CNT actuator, the actuation behavior of the electrothermal actuator, driven by a square wave voltage alternated between 0 and 7 V at a frequency of $f$, was recorded by a digital camera. As mentioned earlier, the two top ends of the U-shaped actuator were fixed at the edge of quartz chip connected to the power supply via sliver paint. The deflection of free end of the actuator was then measured by directly counting on the pictures of its initial and excited states (Figure 2e). When the applied $f$ is higher than a certain value, the cooling effect of the surroundings will not be efficient enough for the recovery of actuator, leading to a reduction of its amplitude. Accordingly, the ultimate work speed of this actuator can be extracted from the amplitude–frequency

Figure 2. Performance of VO$_2$ NA/CNT actuator. a) Schematics of VO$_2$ NA/CNT actuator upon the temperature change from 25 to 70 °C. In the inset figure, the upper panel is the cross section of the device and the arrows show the tensile strain of the VO$_2$ NA film upon cooling. Once the ambient temperature is lower than $T_c$, VO$_2$ NWs undergo a rapid expansion along the $c_R$-axis by $\approx$1%, which forces the whole device to bend toward the CNT side. b) $D/L$ ratio of VO$_2$ NA/CNT actuator as a function of ambient temperature during a heating–cooling cycle. The optical images of the actuation of VO$_2$ NA/CNT bimorphs after: c) heat (scale bar, 10 mm), d) laser irradiation (scale bar, 5 mm), and e) Joule heat (scale bar, 5 mm). The inset figures of parts (c–e) show schematics of the corresponding devices. The red star in part (d) indicates the irradiation position of the laser beam. f) Normalized tip displacement of the VO$_2$ NA/CNT actuator triggered by Joule heat as a function of driving frequency.
curve, as shown in Figure 2f. It is concluded that the −3 dB attenuation frequency of VO₂ NA/CNT actuators (the frequency at 1/√2 of the maximum amplitude, also called cutoff frequency) is approximately 15 Hz, corresponding to a response time of ≈66 ms. The values seem to be uncompetitive compared with typical VO₂ bimorph microactuators or the single-crystalline VO₂ actuator (≈kHz). The rapid amplitude reduction may be attributed to the centimeter-scale size of as-fabricated actuators, which dramatically increases the heat capacity. Ma et al. demonstrated a polycrystalline VO₂/CNT bimorph actuator at a millimeter scale, which also had a relatively low −3 dB frequency of ≈80 Hz. Therefore, we believe that the large size can partly limit the high-speed work of the flexible device. However, the VO₂ NA/CNT actuators demonstrated superior response time to many existing flexible mechanical devices with centimeter-scale size that usually require several seconds to be activated.

To have a clear view of the characteristics of VO₂ NA/CNT actuators, a comparison was drawn with other flexible actuators in Table 1. Like all other VO₂-based actuators, the VO₂ NA/CNT bimorph actuator could be triggered by multiple external stimuli of light, heat, and electricity. There was no evidence of degradation in the amplitude after working for up to 1 million cycles (Figure S7, Supporting Information), which suggests a long lifetime and high reliability. In contrast to other typical VO₂ actuators, the centimeter-size scale of as-fabricated VO₂ NA/CNT structure can greatly broaden the applications for newly VO₂-based mechanical devices. In addition, the calculated total strain of the VO₂ NA film along the longitudinal direction of device reaches ≈0.614% (see details in Section S7, Supporting Information); this is higher than the one for polycrystalline VO₂ thin film (≈0.3%) generating a work density as high as 2.64 J cm⁻³. These findings verify that the VO₂ NA/CNT actuator utilizes the excellent mechanical properties of single-crystalline VO₂ nanobeam for large-scale thin film devices, providing a strategy to overcome the intrinsic limit of traditional polycrystalline VO₂ thin film-based devices. Nevertheless, a large frequency loss was observed in VO₂ NA/CNT actuator, because, in centimeter-scale devices, the heat capacity of the system is dramatically increased which slows down the energy transfer magnitude during the actuation process. Despite the frequency loss, it is still evident that the response of VO₂ NA/CNT actuators is faster than most of existing flexible actuators (Table 1) with insect-scale. In summary, among most of centimeter-scale flexible devices, the VO₂ NA/CNT actuator demonstrates an overall superiority, including remarkable work density, reliable lifetime, multiple trigger modes and competitive work speed.

The alignment of VO₂ NA film has a significant role in the distinctive anisotropy of VO₂ NA/CNT bimorph actuator, so it is expected that the actuator shows a dramatic cutting direction-dependent bending behavior. A series of belt actuators were fabricated with various cutting angles (θ); θ is defined as the angle between the longitudinal direction of the device and the alignment direction of VO₂ NAs (Figure 3a). It was discovered that upon the increase in θ, the actuator bent along the NA alignment direction instead of the device longitudinal direction. As a result, the whole bimorph belt twisted off the longitudinal direction as shown in Figure 3b and its amplitude along the original direction reduced accordingly. Once θ reached 90°, the strain of VO₂ NA only worked along the radial direction of the belt device; in another word, its actuation was almost completely hampered. Figure 3c shows the analysis of the strain distribution of twisted device, showing that the component of the strain along the longitudinal direction of device can be expressed as εₘₐₗ₉ = εₜₜₒₜₜ × cosθ. Because the amplitude of the bending actuation l is approximately proportional to the strain change of the device, it is easy to obtain an approximate expression of l = l₀ × cosθ, where l₀ is the amplitude at θ = 0. The calculated formula fits well with the experimental results (Figure 3b). Notably, the VO₂ NA/CNT actuator with a long length (over 5 cm in this case) could naturally form a helix shape driven by the unique cutting direction-dependent twisting (Figure 3d). The spring-like structure of VO₂ NA/CNT bimorph at room temperature trended to relax to the straight state across the MIT upon heating, decreasing the number of coils. This discovery shows that the remarkable anisotropy property of VO₂ NA/CNT bimorph film brings extraordinary advantages to the design of actuators which greatly enriches the function of

| Actuator | Size [μm] | Cutoff f [Hz] | E [%] | Work density [J cm⁻³] | Trigger mode | Wireless control |
|----------|-----------|---------------|-------|------------------------|--------------|-----------------|
| VO₂/Cr bimorph nanobeam actuators | 50–200 | 1000 | 1 | 7 | Electricity, heat, light | Yes |
| VO₂/Cr bimorph thin film actuators | 50–300 | 6000 | 0.3 | 0.63 | Electricity, heat, light | Yes |
| VO₂/CNT-based thin film actuators | 50–1000 | 35–6000 | N/A | N/A | Electricity, heat, light | Yes |
| VO₂ NA/CNT actuator (this study) | >10⁴ | 15 | 0.614 | 2.64 | Electricity, heat, light | Yes |
| V₂O₅-based actuator | >10⁴ | 0.4 | 0.21 | N/A | Heat | No |
| MoS₂-based actuator | >10⁴ | >2 | 0.8 | 0.081 | Electricity | No |
| Ni(OH)₂-NiOOH-based actuator | >10⁴ | >0.1 | 0.3 | 0.1 | Heat, light | Yes |
| IPMC³ actuator | >10⁴ | <5 | <2 | ≈0.01 | Electricity | No |
| Carbon-polymer bimorph actuators | >10⁴ | <1 | N/A | N/A | Electricity, heat, light | Yes |
| PVD²⁵-based robots | >10⁴ | 3–200 | N/A | N/A | Electricity | No |
| Silicone elastomer-based magnetic robot | >10⁴ | ≈40 | N/A | N/A | Magnetism | Yes |

²⁵IPMC: Ionic polymer-metal composites; ²⁵PVD: Polyvinylidene difluoride.

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**Table 1.** Existing flexible actuators.
devices: both bending and twisting actuators can be facilely made by focused laser beam tailoring with different cutting angles. This setup is much more convenient than complex designs using time- and cost-consumed MEMS processes.

Good flexibility and large size of as-prepared VO2 NA film enables very convenient modulation in the initial state of the actuator, thus the compensation of strain can be facilely achieved by folding the device before annealing. Despite the inevitable performance loss due to the perturbation of external strain, different degrees of the pretreatment greatly enrich the actuation modes of the flexible actuator, e.g., unidirectional bending from zero curvature, bidirectional bending, to meet the requirements of various application conditions (detailed discussion can be found in Section S8, Supporting Information). Moreover, the large-scale device allows the facile structural design by applying the direct laser writing techniques on VO2 NA/CNT bimorph films. Therefore, various devices with versatile applications can be easily fabricated (see the clips in Movie S1 and S2, Supporting Information).

Swift movement and precise operation are two basic requirements of soft robots. Furthermore, photo-driven soft robots, that can sensitively respond to the light stimuli, are highly desired owing to increasing demands on wireless control and accurate location guidance. An arched VO2 NA/CNT bimorph crawling robot is shown in Figure 4a. With the illumination of a strong white light to drive the MIT of VO2, the robot bent with the front leg drawing back and the rear leg moving forward. Because of the specific shape shown in the figure, the rear leg of the robot had a tight contact with the substrate and its front leg was almost suspended. This means that the front leg was free to move, whereas the rear leg could be limited by the frictional force from the substrate. Upon the removal of light, the robot recovered to the relatively flat state, where the rear leg remained at the original location and the front leg moved forward. After a complete movement cycle, the robot moved 0.6 cm and, by considering its cutoff frequency of \( \approx 15 \) Hz, its theoretical crawling speed reached to 9 cm s\(^{-1}\). Due to the unsatisfactory heating control in real measurements, the response time for a complete actuation cycle of the VO2 NA/CNT actuator was elongated to \( \approx 0.3 \) s, indicating that the practical crawling speed was \( \approx 2 \) cm s\(^{-1}\). This is comparable with the recently reported ink-polyethylene terephthalate (PET)-acrylic tri-layered photothermal actuator (2.6 cm s\(^{-1}\)) and superior to other photothermal crawlers, such as a reduced graphene oxide-carbon nanotube/polydimethylsiloxane (rGO-CNT/PDMS) soft robot (1.6 cm s\(^{-1}\)) and polydopamine-modified reduced graphene oxide/Norland optical adhesive-63 (PDA-RGO/NOA-63) actuators (\( \approx 0.1 \) cm s\(^{-1}\)).

The mechanical transfer of small objects is another essential topic of soft robots. Figure 4b,c shows two fundamental light-driven mechanical behaviors of VO2 NA/CNT robots that can be used for mass transfer, lifting and gripping. Figure 4b shows that 0.7 mg of VO2 NA/CNT actuator was utilized to lift an object weighing \( \approx 20 \) mg (30 times heavier) within 6 s. The mechanical gripper in Figure 4c worked on a copper strip that is 50 times heavier than itself and completed a grip-transfer-release cycle from one side to the other side of a 5 cm-long quartz boat.

To meet different requirements of specific operations, the initial state and actuation modes of the aforementioned proposed devices were directionally modified via simple mechanical pretreatments as mentioned in the last paragraph. Occasionally,
some specific applications may oblige some demands on the appearance of robots, especially in some biomimetic applications. Figure 4d,e shows that the modern laser writing techniques can simply create the required appearance and function modification of the VO2 NA/CNT flexible robots for their specific uses, such as wings of flying robots and clam-like mechanical locks for remote mass delivery. In summary, the multiple trigger modes, readily editable shapes and actuation modes, and competitive actuation performance of the VO2 NA/CNT bimorph actuator contribute to its great potential for modern robotics with extensive mechanical applications.

3. Conclusion

We developed an insect-scale soft robotic platform with super-aligned VO2 NA/CNT bimorph films. Due to the large longitudinal strain of super-aligned VO2 NA film, the inset-size, flexible, VO2/CNT actuators were fabricated, and demonstrated more attractive actuation performance than most of flexible centimeter-size actuators. They were characterized with the giant D/L ratio (=0.83), high work density (=2.64 J cm⁻³), excellent lifetime (>10⁶ cycles), competitive work speed (=15 Hz), and rapid response to multiple stimuli (i.e., heat, light, and electricity). These results reveal that the performance of VO2/CNT actuators was comparable with single-crystalline VO2-based actuators, and thus demonstrated the successful strategy of utilizing the superiority of crystalline VO2 NWs in macroscopic devices. The anisotropy feature of the VO2/CNT bimorph films enabled the facile manufacturing of bending and twisting devices by laser tailoring, which broadened the applications and simplified the functionalization compared with conventional microfabrication techniques. Here, we developed a light-induced untethered robotic platform based on the flexible highly anisotropic bimorph films by exhibiting the applications in biomimetic crawler, lifter, gripper, wing of flying robots, minilock, and torsional robot. Our developed strategy (utilizing the intrinsic properties of VO2) can pave the way for future untethered and versatile insect-scale soft robotics with superior performances in macroscopic mechanical devices.

4. Experimental Section

Synthesis of H₂V₃O₈ NWs: 0.1 g V₂O₅ (purity >99%) and 0.022 g C₆H₅O₂·2H₂O were mixed in 100 mL deionized (DI) water and stirred for 2 h to form a uniform orange suspension. The mixture was transferred to a 100 mL-poly(paraphenylene) container, then sealed in a stainless autoclave. The autoclave was heated up to 260 °C and kept at this temperature for 36 h. After the reaction, the autoclave was air-cooled to room temperature. The precipitates in the container were collected by filtration. The final products were washed with DI water, alcohol, and acetone for several times, respectively, and then dried in vacuum at 60 °C for 10 h.

Self-Assembly of H₂V₃O₈ NWs: First, a certain amount of H₂V₃O₈ NWs and polyvinylpyrrolidone (PVP) powder were added to DI water and stirred for 2 h to form a homogeneous suspension (2 mg mL⁻¹ H₂V₃O₈ and 5 wt% PVP). Second, 3 mL suspension, 10 mL DI water, and 5 mL alcohol were sequentially added to 100 mL chloroform in a cubic glass container (5 × 5 × 5 cm³) underwent a strong stirring, and then awaited until the shining green aligned films appeared on the surface of liquid. Finally, a smooth substrate, covered by a layer of CNT film with a designed pattern, was used to collect the green NA film. The H₂V₃O₈ NA/CNT bimorph structure was washed with acetone to remove the residual PVP.

Postannealing of H₂V₃O₈ NAs: The bimorph structure was placed in the middle of a tube furnace. The system was heated up to 500 °C within 20 min and kept at this temperature for 20 min, during which the gas pressure of the chamber was kept at ≈300 Pa.

Materials Characterization: The phase structure was tested by D8 ADVANCE ECO (Bruker) X-ray diffractometer. Raman spectra of samples were obtained by a HORIBA Raman spectrometer (LabRAM HR Evolution), where the excitation wavelength was 532 nm. The morphology
of samples was examined by a Phenom SEM (ProX). A FEI Tecnai F30 TEM was used to characterize the crystal structure and crystal direction of samples.

**Measurements of the Actuation Performance**: The bimorph actuator was attached to a quartz plate and heated through a heating stage from 25 to 95 °C, and the photos were taken at every 5° change by Huawei honor 9 cell phone, after which we used Photoshop software to measure the displacement of actuator. The equation used to calculate the strain is as follows:

\[
\varepsilon = \frac{2d\delta}{d^2 + L^2}
\]

(1)

where \(\varepsilon\) is the strain, \(d\) is the thickness of actuator, \(\delta\) is the amplitude of actuation, and \(L\) is the actuator length.

**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.

**Keywords**

bimorph actuators, insect-scale soft robotics, metal–insulator transitions, vanadium dioxides

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