1 **Title** Self-actuating origamis realized by independently printable and controllable

2 stimuli-responsive creases

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9 **Abstract**

10 Flexible origami structures can mimic the complicated motions of small creatures that are

11 otherwise difficult to be achieved by rigid robots with limited degree of motion freedom.

12 However, actuating origami structures in a compact and self-contained way has been a critical

13 challenge. Here, we demonstrate a versatile approach of actuating origami micro-robots by

14 printed self-folding creases made of a type of stimuli-responsive transition metal

15 hydroxides/oxides that can undergo large actuation under electrochemical or light stimulations.

16 Two enabling technologies are pivotal: (i) a microfluidic electrochemical writing method to

17 selectively print the stimuli-responsive material (SRM) at the actuating creases to enable them to

18 self-fold independently "on demand", and (ii) a micro-scale riveting method to provide strong

19 adhesion of the SRM on the origami body. Such strategies allow the successful construction of

20 actuating creases made from different stimuli-responsive transition metal hydroxides/oxides that

21 can self-fold into curvature exceeding 1 mm^{-1} under low-intensity visible-light stimulation in

22 ambient conditions, or low-potential electrochemical stimulation in electrolytic environments,

23 with response time as fast as in seconds. Based on the high performance of such active creases,

24 complex miniaturized origami designs powered by hinges activated in an independently

25 controllable way are demonstrated, including self-folding Miura and a full micro-robotic hand

with independently programmable finger joints. These results prove a new, versatile paradigm for robotics, where a transferrable approach is applicable to design and fabricate a wide variety of customizable micro-robots with compact construction and complex motions using different stimuli-responsive ceramic-based materials.

Graphic abstract
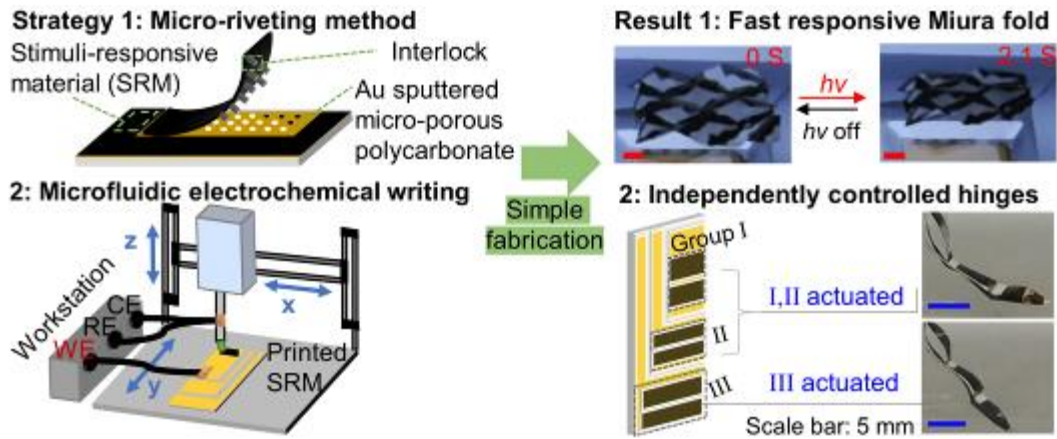
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MAIN TEXT
Introduction

Origami-robots are regarded as next-generation machines that can shape-transform, walk/crawl, and perform tasks over a large domain of the configurational space [1, 2, 3, 4]. The major components of origami designs involve a supporting structure that allows folding and actuating units that induce the shape transformation [5, 6]. Earlier designs of origami robots are powered by discrete motors [7], fluid [8, 9] or magnets [10, 11] which require bulky backing systems or external magnetic field generators, respectively. To increase the compactness level for the complex origami structures containing many faces and hinges, origami designs powered by stimuli-responsive materials (SRMs) have emerged [12-20]. For realistic applications, however, the SRM chosen should be reversible and fast responding, say, in seconds, and the stimuli should be low-power and easily integrable into system designs. Origami designs involving one-way shape memory materials [12], polymers or gels [13, 14, 15] are irreversible in motion or exhibit slow responses from several minutes to hours. Deploying actuating materials responsive to temperature [16, 17, 18] or humidity [19] changes are less practical as these stimuli are less easily integrated into or delivered to compact systems, than stimuli such as electric or light signals. Graphene-based origami robots driven by near infrared (NIR) light can perform fast shape transformation, but their fabrication and stimulation involving graphene and NIR are rather complex [20].

Despite the few SRM-powered origamis demonstrated so far, they were designed and fabricated based on protocols specific to the SRM chosen, and hence, a versatile paradigm that is transferrable to different SRMs and designs is critically lacking. In this work, we demonstrate a versatile and simple approach for actuating origamis that has never been attempted before (Fig. 1). We construct stimuli-responsive self-folding creases for actuating origamis, as per a "minimalism" concept. An origami robot, by definition, is a structure that changes shape by folding of its creases, and so the "minimalist" design would be to have just the creases, rather than

the whole body, made of a high-performing SRM that enables them to self-fold efficiently upon receiving external stimuli (Fig. 1B). Such a design concept, in conjunction with a high-performing SRM, should lead to origamis that are most compact, but its realization would imply overcoming two immediate challenges:

(i) How to integrate the SRM into the specific locations of the creases "on demand", so that, for instance, the creases can be stimulated independently of one another, or different crease patterns can be easily made with a single setup?

(ii) The origami substrate can only be compliant materials like polymers, because metals or ceramics would crack or fatigue-fail on repeated folding. Therefore, it is of paramount importance to ensure enough adhesion between the polymeric substrate and the chosen SRM, so that the latter would not delaminate on repeated folding of the crease.

In this study, we aim to demonstrate a versatile approach for solving the above two problems which is in principle applicable to a wide variety of ceramic-based SRMs that can be fabricated by electrodeposition. For the purpose of illustration, we choose a recently discovered type of stimuli-responsive transition metal hydroxides/oxides [21, 22] including nickel hydroxide/oxyhydroxide (NHO, Fig. 1A) or manganese oxides [23], that are fast responding to mild electrochemical or light stimuli. For solving challenge (i) mentioned above, we demonstrate a microfluidic electrochemical writing method for the "on demand" writing of the SRMs on the origami substrate (Fig. 1C(i)). Existing fabrication methods such as selective-laser sintering or ink-jet printing of a ceramic precursor followed by post-treatment [24, 25], or masked electrodeposition [26, 27], can result in ceramic patterns, but the precursor method involves additional sintering which is not applicable to ceramic patterns coated on polymeric origami substrates, and masked electrodeposition requires a new mask for each pattern to be made. Here, we demonstrate a direct and simple open-electrodeposition method, and apply it to the SRMs. For solving challenge (ii) above on adhesion between the SRMs and the origami substrate, we

demonstrate a micro-riveting concept (Fig. 1C(ii)), in which the hydroxide/oxide SRMs forms strong locks with micro-porous polycarbonate (MPPC) substrates to provide the adhesion needed for the folding process. These methods are used to successfully fabricate pre-designed crease patterns of SRMs to make self-folding origamis driven by either electrochemical or visible-light stimulations (Fig. 1B). In Results below, the SRMs are first described, followed by the enabling technologies and resultant origamis.

Results

1. The active stimuli-responsive materials

The key concept in the present work is to actuate origamis by independently printable and controllable stimuli-responsive creases, and we demonstrate this using a type of transition metal hydroxides or oxides for the creases that have been recently discovered to exhibit significant volume shrinkage on mild oxidizing potential charging in alkaline electrolytes [21, 23], or under low-intensity light illumination in ambient conditions [22]. In addition to their high-performing actuation behavior (details given below), these materials are also low-cost and easily printable on substrates using electrodeposition (see Methods), so they are ideal for making self-folding origami creases. In below, due to space limitation, we illustrate the working principles using results primarily from nickel hydroxide/oxyhydroxide (abbreviated as NHO, see Fig. 1A), although we also fabricated a robotic hand made of independently printed and controlled MnO_x muscles as shown in Movie S1 and fig. S4A. Both NHO and MnO_x exhibit an electrochemical actuation behavior under mild potential stimuli in alkaline media [21, 23], and in addition, NHO exhibits a light-triggered actuation behavior under low-intensity visible-light stimuli in ambient conditions [22].

Although the actuation behavior of transition metal hydroxides/oxides has been reported before [21, 22], how their microstructure changes in response to stimuli is not clear. Therefore, to

illustrate the mechanisms of the actuation, we carried out detailed microstructural characterization on NHO, which is the main material presented hereafter. As shown in Fig. 2A, cyclic voltammetry shows that the NHO material can be oxidized on potential larger than ~0.4 V and reduced at potentials smaller than ~0.3 V against Ag/AgCl reference electrode in 1 M NaOH, depending on the scan rate. Larger scan rates can lead to higher current peak (absolute value) and lower curvature (Fig. 2A and S6). A larger range of scan rate was also studied for the same actuator at a fixed potential window, and again, the curvature drops at increasing scan rate because of incomplete and suppressed redox reaction at higher scan rate (Fig. S7). Figure 2B(a) shows the grazing-incidence X-ray diffraction (GIXRD) spectra of the oxidized and reduced states of NHO. The GIXRD patterns of these two states show characteristic changes near 34° and 37°, shown in a magnified scale in Fig. 2B(b), due to the (100) β-Ni(OH)$_2$ (2.63 Å) and (101) β-NiOOH (2.43 Å) diffractions, respectively [28, 29]. On changing from the reduced to oxidized state, the (101) β-NiOOH peak near 37° emerges, whereas the (100) β-Ni(OH)$_2$ peak near 34° subsides, indicating that the oxidation is due to the transformation from β-Ni(OH)$_2$ to β-NiOOH, as shown in Fig. 1A(i). β-NiOOH is known to have a smaller crystal volume than β-Ni(OH)$_2$ [21, 22], and this explains the volume shrinkage on oxidation.

Another characteristic of the GIXRD patterns of both the reduced and oxidized states is a broad peak at 2θ ~18°, which arises from the (001) planes of both the Ni(OH)$_2$ and NiOOH hexagonal crystal structures [28, 29]. Fig. 2B(a) shows that, on changing from the reduced to oxidized state, the (001) peak becomes sharper, and the 2θ value of ~18° corresponds well to the wavy lattice fringes of ~4.7 Å in the oxidized state directly observed by HRTEM in Fig. 2C. The wavy nature of the (001) lattice fringes are characteristic of turbostratic crystal structures due to the intercalation of H$_2$O molecules into the lattice [29, 30] – a fact confirmed by a large H$_2$O absorption peak observed in Fourier-transform infrared spectroscopy measurements [28]. The observed sharpening of the (001) peak indicates a drop in turbostraticity, or loss of intercalated

water from the lattice, on oxidation. As water is lost from the crystal structure, the volume should shrink, and this is likely a second reason for the observed shrinkage on oxidation of NHO [21].

As for light actuation, in situ GIXRD experiments were carried out with a visible light source placed inside the diffractometer to excite the NHO sample in the oxidized state, which is the as-fabricated state of the NHO in all the light actuation tests in this work (see Methods). The GIXRD results in Fig. 2B(c) and (d) show that during X-ray scanning at a very slow rate of 0.05°/min without or with visible light illumination at intensity ~50 mW/cm^2, a noticeable change is a slight right-shift of the right edge of the (001) broad peak at 2θ ~18° (Fig. 2B(d)). The previously described changes near 34° and 37° on changing from oxidation to reduction were not noticeable during light illumination on the oxidized sample in Fig. 2B(b), indicating that the light excitation only slightly decreases the interplanar spacing of the (001) basal planes, but does not electrochemically reduce the sample. The right shift of the 2θ value on light stimulation was about 0.17°, and from Bragg's law, the (001) plane spacing is reduced by about 0.91% at ~50 mW/cm^2 illumination. Earlier work has indicated that the light induced shrinkage of NHO only occurs in ambient conditions with regular humidity, but not in a vacuum environment, and the material also exhibits actuation on humidity changes of the environment [21]. The results in Fig. 2B(d) now indicate that light illumination reduces the (001) spacing, evidently due to a light-induced loss of the intercalated water molecules from the crystal structure. The light only causes the right edge of the (001) peak to shift right, presumably because visible light can only penetrate into a very shallow layer of the sample surface where the (001) spacing is smaller due to dehydration, while the left edge of the (001) X-ray peak is dominated by deeper layers reachable by X-ray.

2. Enabling technologies

2.1 Substrate/interface engineering

The key concept of the present work is to integrate the SRM into a suitable origami substrate at specific locations to make self-folding creases (Fig. 1B). As mentioned above, soft polymeric instead of metallic or ceramic films are chosen as the origami substrates since polymers are generally soft enough to be repeatedly foldable. Furthermore, according to Timoshenko's theory [*31*], for an actuating layer of thickness h_a and elastic modulus E_a coated on top of a passive substrate layer of thickness h_s and elastic modulus E_s, the actuation curvature is given by (see Section S1):

$$\kappa = \frac{6h_a(h_a + h_s)}{E_a h_a^3 + E_s h_s^3} \sigma_a \tag{1}$$

where σ_a is the intrinsic actuating stress of the active layer. Eqn. (1) indicates that large actuation will be achieved by lowering the stiffness of the substrate.

In this work, a type of thin microporous polycarbonate (MPPC) membranes with pore size 3 µm (unless otherwise stated) and thickness $h_s = 10$ µm was used as the origami substrates. Prior to electrodeposition of the SRM, the MPPC membranes were pre-sputtered with a thin atomic layer of Au (see Fig. 1C and inset in Fig. 3D), which served not only as the conductive electrode for the electrodeposition, but also increased the adhesion between the hydroxide or oxide SRM, and the MPPC. The porous nature of the MPPC membrane serves two purposes. First, the presence of the pores lowers the effective modulus, and hence larger actuation can be achieved according to eqn. (1). Secondly, as the SRM material is deposited onto the MPPC membrane, some of it will grow into the micro-pores of the membrane to form micro-scale rivets as shown in Figs. 3A and 1C(ii), so that the SRM layer will adhere firmly to the substrate. After short electrodeposition for 0.5 h in the case of NHO (Fig. 3A(i)), some of the pores in the MPPC membrane were covered by NHO but others were unfilled, and prolonging the electrodeposition to 2 h (Fig. 3A(ii)) resulted in all pores covered by an NHO layer. To reveal the growth of the NHO material into the pores of the MPPC substrate, peel tests were performed (Fig. 1C(ii)). Peeling off an NHO layer

electrodeposited for 2h from the MPPC membrane revealed the deep deposition of the NHO material into the cylindrical pores as shown in micrographs (III) and (IV) in Fig 1C(ii).

To show that the micro-riveting strategy is effective in improving the actuating performance, control experiments were carried out on actuators made by electrodepositing NHO onto non-porous polycarbonate (PC) membranes as well as porous ones with different pore sizes. On non-porous PC substrate, the actuation is very small, due to the significant delamination of the active material which can be observed just after five cycles of actuation when the active material was deposited for 0.5h (inset in Fig. 3B). To figure out the influence of the substrate pore size on the adhesion and actuating performance, PC substrates with pore sizes of 0.03, 0.2, 3 and 10 μm were electrodeposited with the NHO material for 0.5 h, 1h and 2 h, as shown in Fig. 3B. Actuators made on the substrate with a pore size of ~0.2 μm deliver the best actuating performance, and for the same pore size, prolonging the electrodeposition of the active material from 0.5 h to 2 h leads to improvements in the actuation performance, due to more and deeper filling of the NHO into the substrate pores as shown in Fig. 3A(i) and (ii). To assess the long-term reliability of the micro-riveted NHO/MPPC interface, bilayered actuators made with uniform NHO electrodeposited (for 2 h) onto MPPC substrates were subjected to repeated light and electrochemical stability tests (see Materials and Methods). Figure 3C shows the change of the bending angle of the actuators over 3000 cycles. The actuation performance was very consistent over long usage under both light and electrochemical stimuli, and only began to degrade after around 2700 cycles for the case of electrochemical actuation, due possibly to cracks formed during repetitive ultra-large motions. Before the final degradation, there was no significant sign of delamination of the NHO material from the MPPC substrate, thus indicating a strong interlocking effect of the micro-rivets into the porous substrate especially at long electrodeposition time.

To show the advantageous effect of MPPC as the substrate material, NHO layers of different thickness h_a in the range $0.6 - 2.2$ μm were deposited onto 10 μm thick MPPC membranes (see

Sections S2 and S3). In Fig. 3D, the bending curvature κ observed under electrochemical actuation tests conducted in 1 M NaOH electrolyte and light stimulation of around 20 mW/cm^2 is plotted against the factor $6h_a(h_a + h_s)/(E_a h_a^3 + E_s h_s^3)$ according to Eqn. (1). It can be seen that the data fall onto straight lines in agreement with Eqn. (1). Furthermore, data from similar actuators made by depositing NHO onto Ni substrates (with much higher Young modulus of ~220 GPa than the ~2.3 GPa for MPPC) are also plotted in Fig. 3D for comparison [21]. It can be seen that the achievable bending curvature on Ni substrates is only up to about 0.2 mm^{-1}, while this can reach 1.2 mm^{-1} on the MPPC substrates (see Movie S2). As analyzed in Section S2, under electrochemical potential drive of less than 1 V in 1 M NaOH electrolyte, NHO can deliver an intrinsic actuation stress of ~20 MPa over strains up to 1% and work density up to ~100 kJ/m^3, which outperforms human muscles with work density of ~40 kJ/m^3 [32]. Under low visible light stimulation at ~20 mW/cm^2, NHO can deliver an intrinsic actuation stress of ~11 MPa at ~0.5% strain with work density about 28 kJ/m^3 (see Section S3).

2.2 Selective printing of actuation patterns

To print the SRM onto the origami substrate at specific locations where it is needed, the first method used was masked deposition. Fig. 4A shows this process for the case of the "Miura" origami structure shown in Fig. 1B(ii, iii), where two sets of target NHO crease patterns need to be electrodeposited on the top and bottom sides of an MPPC membrane. However, to improve the flexibility of pattern design and fabrication, a special microfluidic electrochemical writing method involving the local microfluidic delivery of electrolyte [33] was also developed for both the NHO and MnO$_x$ material, as shown in Figs. 1C(i) and 4B. In this method, the required electrolyte for the SRM electrodeposition (see Materials and Methods) is delivered locally to the desired location of the conductive substrate via a pump-driven syringe needle which itself is also conductive. A gap is maintained between the needle tip and the substrate, so that a micro-volume of the liquid

electrolyte is held between the two by surface tension effects. Application of a suitable potential difference between the conductive syringe needle and the substrate then triggers the electrochemical formation of the SRM within the small electrolyte volume in contact with the substrate, and scanning the needle over the substrate allows an SRM pattern of any geometry to be written on the substrate. Repeatedly scanning over the same place would also increase the thickness of the SRM deposited.

3   Origami actuator performance

3.1 Self-folding origami structures triggered by light and electrochemical stimulations

The performance of a single crease design under light and electrochemical stimuli is shown in Fig. 1B(i). The samples were fabricated by electrodepositing a 4 mm-wide strip of the NHO material across the width of a rectangular MPPC membrane substrate measuring 16 mm by 8 mm (see Materials and Methods). After the electrodeposition, residual stress caused the membrane to bend to form a smooth crease, as shown in Fig. 1B(i). Under light illumination or oxidizing potential charging, the creases self-actuated in the direction that corresponds to the contraction of the coated NHO material. The bending angle could be up to 120° under light intensity of ~40 mW/cm^2, or 160° over the potential window from 0.8 V to -0.2 V with a scan rate of 25 mV/s (see Movie S3). For light actuation, the actuating rate increases from 8.7 deg/s to 60 deg/s for light intensity from 5 mW/cm^2 to 40 mW/cm^2, and the corresponding recovery rate increases from 6.5 deg/s to 22.5 deg/s. The single origami crease design was triggered by step potential under -1 V for 0.5 s to actuate and 1 V for 1 s to recover in 1 M NaOH electrolyte, or under illumination of vis light intensity at ~25 mW/cm^2 on for 0.5 s to actuate and 1 s off to recover for both 1000 times. Under both types of stimuli, the actuation performance was very stable over the 1000 cycles (Fig. S8).

Based on the single NHO creases, a variety of self-folding origami structures were fabricated and tested. Fig. 5 and Movies S4, S5 and S6 show the self-folding response of Miura origami structures under the stimulation of visible light and electrochemical stimulation. These structures were printed using the method shown in Fig. 4A, and to facilitate their subsequent self-folding action under stimulation of the active NHO, the MPPC substrates were pre-folded along the crease patterns after their printing. In the present work, all the as-fabricated NHO material was in the oxidized state (see Materials and Methods) so that for light actuation, the initial state would *contract* on light stimulation, and for electrochemical actuation, the initial state would *expand* on application of a *reduction* potential (see Fig. 1A). Therefore, to allow the as-fabricated Miura structures to self-fold on application of either light or reduction-potential stimuli, the pre-folding directions were opposite between the two cases: for light stimulation, the solid-line creases printed on the top side of the MPPC membrane in Fig. 4A became folded valleys while the dashed-line creases printed on the bottom became folded mountains when viewed from the top, and for the electrochemical actuation, the folding sense was reversed. In this way, the Miura will shrink on either application of a reduction potential (Fig. 1B(ii)) or light illumination (Fig. 1B(iii)).

To quantify the Miura actuation, Fig. 5 (A, B) illustrate the schematic of the Miura fold. The parameters α, l_1 (along x direction) and l_2 (along y direction) completely define the configuration. The recovered (stimuli off) and actuated (stimuli on) states are shown in Fig. 5B where widths l_r (at recovered state) and l_a (at actuated state) define the device strain ε along the l_2 direction according to $\varepsilon = (l_r - l_a)/l_r$. Similarly, lengths l'_r and l'_a define the device strain ε' perpendicular to the l_2 direction according to $\varepsilon' = (l'_r - l'_a)/l'_r$.

For the light actuation, the Miura structure was illuminated by an LED light source with a nominal power rating of 30 W, and a camera was used to record the motion of the structure (see fig. S5A). The setup was placed in ambient laboratory conditions of 24°C temperature and 65%

relative humidity (RH). Figure 1B(iii) shows the natural and actuated shapes of the Miura structure. When the light source was switched on to give an intensity of 120 mW/cm^2 at the Miura structure, the latter contracted to a steady state in around 2 seconds (see Movie S4). As the light was switched off, the Miura structure recovered to the original shape, and the process was highly repeatable. The device strains ε and ε' along and perpendicular to the l_2 direction are shown in Fig. 5C. The distance of the LED light from the Miura structure was varied to give different light intensities at the origami actuator, which were measured by a light meter (see Materials and Methods). Fig. 5D indicates that the light intensity has a profound effect on both the device strain and the actuation response time of the actuator. At intensities higher than ~100 mW/cm^2 (~1 sun), device strains of ~60% can be achieved in less than 5 seconds; for example, at 150 mW/cm^2 the actuation can be completed in less than 1 second (Movie S5). At illumination intensities lower than ~1 sun, the device strain was lower, and the response was also slower. The recovery time increases from 3 to 10 seconds as the light intensity increases from 30 to 150 mW/cm^2.

To illustrate electrochemical actuation, a Miura fold was submerged in 1M NaOH and stimulated by a step reduction potential (-0.2 V relative to Ag/AgCl electrode) to actuate, and then a step oxidization potential (0.8 V relative to Ag/AgCl electrode) to recover (Movie S6). The device strains along and perpendicular to the l_2 direction are also shown in Fig. 5C. The Miura fold was also stimulated by a potential scan from 0.5 V (oxidized state) to -0.1 V (reduced state) at a very slow scan rate of -3 mV/s to ensure quasi-equilibrium at each potential, and the device strain vs potential is shown in Fig 5E. The maximum device strain ε achievable is around 60% under electrochemical stimulation, which is similar to that for light stimulation. However, Fig. 5C shows that the electrochemical actuation is significantly slower than the light actuation (minutes vs seconds).

To illustrate the load lifting capability of the Miura design, a load was suspended on the Miura structure along the l_2 direction. The active weight of NHO is calculated to be 47 mg, by

multiplying its volume (area = 5.6 cm^2, thickness = 2.1 μm) and density ~4.0 g/cm^3 [*34*]. For light stimulation at 120 mW/cm^2, a Miura can lift a weight of ~250 mg, which is a piece of polymeric foam in air, with linear device strain ~0.3, as shown in Fig. 5F and Movie S7. Under electrochemical stimulation by step potential -1 V applied relative to Ag/AgCl electrode in 1M NaOH electrolyte, a similar Miura design can lift a load of ~120 mg, which is a piece of solid plasticine (density ~1.9 g/cm^3) of dry weight 250 mg before accounting for buoyancy, producing linear device strain ~0.2 as shown in Fig. 5G (see Movie S8).

3.2 Fingers with independently controlled joints in response to light and electrochemical stimuli

Amongst SRM-driven origami designs published in the literature, a capability that has never been reported before is independent control of different hinges in the same origami device. Here, we demonstrate this capability via finger designs with independently controlled joints. These fingers were fabricated using the microfluidic writing method shown in Fig. 4B, where the actuation joints of either NHO or MnO$_x$ were written on isolated conductive areas of Au deposited onto the MPPC substrate. Therefore, by delivering electrochemical or light stimuli to the Au areas individually, the actuation joints can be triggered independently.

For the electrochemical actuation, a finger-mimicking device comprising three "muscle groups" I, II and III is shown in Fig. 6A. Each "muscle group" consists of several actuating strips of NHO written directly onto an Au area pre-sputtered onto the MPPC substrate (see Materials and Methods). The Au pattern served not only as the conductive electrode required for the electrochemical writing of the NHO material, but also as the metallization needed for the independent control of the muscle group on top. In Fig. 6A, each muscle group (I to III) comprises two NHO strips (shown in dark gray) written onto Au domains (shown in yellow) isolated from each another, supported by an underlying MPPC (shown in light gray). In the subsequent actuation test (Fig. 6A, B), electrical connection with the electrochemical workstation

was made to the Au domains to allow the corresponding NHO muscle groups to actuate independently. Under 0.8 V potential with respect to Ag/AgCl reference electrode (RE) in an electrolyte of 1 M NaOH, the NHO muscle group contracted, and under 0.0 V, the muscle group recovered. The bending motion of the robotic finger was captured using a camera, and markers located at specific end points of the muscle groups were used for gait analysis. Fig. 6B, C and Movie S9 show that the independent actuation of the muscle groups allows the finger to adopt different shapes. Furthermore, to illustrate that the concept is versatile for other SRMs, MnO_x – another proven SRM [23]– was printed on MPPC substrates to form electrochemical actuators. The MnO_x actuating patterns exhibit good adhesion with the polymeric substrate, and also demonstrate excellent actuating behavior (see fig. S4 and Movie S11). A full-hand device was made from MnO_x creases on MPPC substrate, as shown in Movie S1, where the fingers can be actuated independently.

To demonstrate independent actuation under light stimulation, another finger design comprising two NHO strips (each 4 mm width) coated onto MPPC pre-sputtered uniformly with Au was made. Two light sources of intensity 30 mW/cm^2 were used to locally stimulate the actuating hinges "on demand" (Fig. 6D). The motion of the finger under four exemplary states of light stimulation is shown in Fig. 6(E, F) and Movie S10.

Discussion

The critical problem of how to actuate origamis in a compact, self-contained way is solved in this work by a minimalist design concept in which high-performing SRMs of transition metal hydroxides/oxides are deployed to make the self-actuating creases. In particular, NHO is one of the cheapest and easily made SRMs that exhibit high actuation performances under both light and electrochemical stimulation, due to a change in the (001) lattice spacing or a volume-changing redox reaction, respectively, as shown in the results in Fig. 2. The folding origamis are made from

microporous polycarbonate membranes on which actuating crease patterns are printed by selective electrodeposition. The micropores on the membranes are critical in enabling the formation of micro-scale rivets after growing in of the NHO material, which then provide an effective means of bonding the active material layer to the substrate. The porous substrate delivers much better actuating performance compared with the non-porous counterpart, demonstrating the effectiveness of the micro-riveting method. Among the pore sizes of 0.03, 0.2, 3 and 10 μm studied, 0.2 μm delivers the best riveting effect and 3 μm also yields comparable results (Fig. 3B); therefore pore sizes ranging from 0.2 to 3 μm are optimum for device design. The smaller pores of 0.03 μm exhibit relatively poor adhesion, because little NHO could be filled into the pores to form strong rivets. The NHO electrodeposited on the substrate with the large pore size of 10 μm also delivers relatively poor actuation performance, probably due to the larger amount of NHO filled inside the passive layer, thus increasing the Young's modulus of the passive layer. Also, since the formation of the NHO actuating layer is influenced by the morphology of the passive layer, larger cracks can be formed inside the actuating layer, thus reducing the strength of the actuating layer and its actuation performance.

A second SRM of MnO_x was also used in the full-hand design in Movie S1, with the same micro-riveting method to achieve sufficient adhesion on MPPC substrates. The micro-riveting method is therefore proven to be a rather general, versatile method deployable to different ceramic-based SRMs. Apart from NHO and MnO_x, a range of other SRMs capable of changing volume in response to environmental stimuli such as temperature [*20*, *35*, *36*, *37*], light [*20*, *38*, *39*] , voltage [*40*] or humidity [*41*] are in existence and may be candidate active materials for self-folding creases. Future work may explore these other SRMs.

Another key enabling technology is the microfluidic electrochemical writing method which allows arbitrary crease patterns of the active material to be written on the origami substrates. In this work, we have demonstrated this method for the two SRMs of NHO and MnO_x, and it should

work in principle for other ceramic SRMs that can be electrodeposited by an electrochemical means. Together with the more traditional bath/masked electrodeposition method, pre-designed active crease patterns that can be stimulated locally and/or independently can be printed, thus allowing complex shape changes. One possibility is to employ machine-learning methodologies to reversely design the optimal active-crease patterns to achieve a particular category of complex motions. Another interesting direction would be Miura robots with gradient or non-uniform active-crease units which may also be independently stimulated. Such designs would involve strained (high-energy) and unstrained (low-energy) substrate states [2], and by exploiting their interplay via independently controlling the crease units, high flexibility in motion control may be achieved.

The thickness of the present origami structures is ~10 μm, which is only ~0.2 % of the planar dimensions of structures (~4 mm). Therefore, the structures can be regarded as "near-zero-thickness surfaces" [42, 43]. In the Miura-fold design, the intersecting area was trimmed to reduce the constraining effects of the interior vertices on the folding motion [43]. The supporting passive membrane was pre-folded manually along the folding paths, which may avoid the singular behavior and help the structure transform into the designed configuration smoothly during the reversible folding process [44, 45]. The present fabrication methods (c.f. Fig. 4) also allow the actuating SRMs to be precisely located at the actuating hinges effectively, and because of their high-performing actuating performance, the origami structures could deliver large folding along the folding lines. However, since a certain width of the SRM is required to achieve sufficient folding along the creases, the printing method may not be suitable for micron-scale origami structures. There are several degrees of complexity for folding, starting from the simple and basic (mountain or valley) folding, which could be stimulated independently, to the Yoshimura units, and to complex folds such as Miura-origami which contains multiple and repetitive units undergoing motion "all at once" when triggered by environmental stimulations [46].

The multi-stimuli responsive nature of NHO enables origami structures to actuate in both liquid (electrochemically stimulated) and ambient (light stimulated) environments. For the Miura folds shown in Fig. 5C, under both stimuli, the eventual device strain can be up to 60 %. However, the actuating strain rate under light stimulation is up to 30%/s (at intensity 120 mW/cm^2), which is much faster than the 0.03%/s under electrochemical actuation. For the light intensity of ~1 sun (100 mW/cm^2), the actuating time is up to 2 seconds, plus ~10 seconds to recover, but it will take around 3.5 min for electrochemical actuation. The sluggish electrochemical actuation of the Miura fold is intriguing, since for bilayered actuators comprising a uniformly coated NHO layer on MPPC (Section S2, fig. S3, Movie S2) the actuation time is much shorter in a few to tens of seconds. The reason for the slow actuation in the Miura case may be due to the poor conductivity and the narrow widths of the NHO material in the crease pattern, and/or a stress effect on the chemical kinetics of the redox reaction which drives the actuation of the NHO material. In both the uniform-coating design in fig. S3 and the Miura fold in Fig. 5, the MPPC substrates had the same thickness (10 μm), but in the case of the Miura fold, there is much less NHO to actuate the substrate, than the uniform-coating case. The resistance stress exerted on the NHO material is significantly higher in the Miura fold, so that the kinetics of the redox reaction may be suppressed. Further research should investigate the mechanics effects on chemical kinetics in a systematic way, for both electrochemical and light actuation.

Compared with electrochemical stimulation, the main advantages of light actuation in the case of NHO are fast response and its wireless nature. Potential applications may include micro-robots for surveillance or inspection in narrow confinements where the robot needs to travel far. The main limitation or challenge is light guide technology needed to incident light specifically on different actuators in a multi-actuator design. For electrochemical actuation, wiring and electrolyte packaging are needed, and the response can be significantly slower. Electrochemically stimulated devices are more suited for stationary applications, while independent control of

different parts is desirable. Examples may include prime movers in small devices, e.g. micro-fans for cooling electronics, micro valves or guides in micro-fluidic channels, transducers for micro-force tensile testers for soft specimens, and so on. Our technique uses inexpensive protocols and reagents. It is easily adaptable and can be deployed to fabricate micro-robots for a wide range of potential applications such as self-charged or integrated sensing actuating systems by combining with other energy storage units [47, 48, 49, 50].

As stated in the Introduction, many of the SRM-driven origami designs in the past exhibited slow responses requiring minutes to hours to actuate [13, 14, 15] (Table S1). Liquid-crystal elastomers show fast responses in seconds [17], but these materials require heat-light coupled pre-programming, and the actuation is triggered by temperature changes which are less convenient to deliver in a compact design, or one in which multiple actuators need to be controlled independently. Graphene oxide which exhibits fast actuation responses in seconds [20] under light, heat or humidity stimuli will be a good SRM for making actuating creases, but the fabrication is complicated (sonication for 100 min, stirring for 12 h, centrifugation, washing, filtration, etc.) and it requires near infrared (NIR) light to actuate. Also, these SRMs may not be easily integrated [15, 20] to make intersecting mountain and valley hinges, and therefore a lot of complex origami structures with high application potential such as Miura-ori and waterbomb may not be achievable [51]. The present transition metal hydroxide/oxide-based SRMs may be more promising in terms of their multi-stimuli response to both voltage and visible light signals, which are easier to deliver and control than heat or humidity changes. They are also fast responding in seconds, and easy and cheap to fabricate. Table S1 summarizes the comparison of various SRMs with the ones studied in this work.

Conclusion

A new concept for origami robotics was demonstrated to actuate micro-robots by stimuli-responsive hinges made of a type of actuating hydroxides/oxides supported on micro-porous polymer substrates. Combining the methods of micro riveting and microfluidic electrochemical writing of the stimuli-responsive hydroxides/oxides, a versatile yet simple paradigm for fabricating micro-robots with fast response and independently controllable degrees of freedom of motion was established. The fabricated stimuli-responsive hinges can be stimulated by visible light of intensities less than 1 sun in ambient conditions, or electrochemical potential of less than 1 V in alkaline electrolytes, to perform reversible shape transformation as fast as in seconds. Based on such self-folding hinges, complex origamis including Miura folds and a micro-robotic hand with independently controllable finger hinges were achieved. The present approach is versatile for different stimuli-responsive materials that can be electrodeposited, and is easily adaptable for the fabrication of compact micro-robots with multi-stimulated, controllable, reversible and fast shape transformation.

Materials and Methods

Nuclepore Track-Etched Polycarbonate Membranes with a diameter of 47 mm and a pore size of 0.03, 0.2, 3 and 10 μm (MPPC membranes) were purchased from Whatman®. Non-porous polycarbonate (PC) membrane of 6 μm thick was purchased from Goodfellow. Nickel sulfate heptahydrate ($NiSO_4 \cdot 7H_2O$), manganese (II) acetate tetrahydrate ($C_4H_6MnO_4 \cdot 4H_2O$) in purum p.a. grade, sodium acetate (CH_3COONa), sodium sulfate (Na_2SO_4), sodium sulfite (Na_2SO_3) in puriss. p.a. grade, and sodium hydroxide (NaOH) in reagent grade, were purchased from Sigma–Aldrich and used as received. An electroless Au-plating solution (Oromerse SO Part B) was obtained from Technic Inc for the Au electrodeposition. Copper (Cu) tape was purchased from 3M. Deionized (DI) water with a resistivity of ~18 megohms·cm was utilized to make solution baths and for rinsing.

Bath electrodeposition of NHO on MPPC membranes

Actuating material NHO was electrodeposited on MPPC membranes using an electrochemical workstation (LK2006A, Lanlike) in a beaker-type electrochemical cell equipped with a working electrode, a platinum mesh counter electrode, and a saturated calomel reference electrode. To metallize the MPPC membranes for the electrodeposition, they were first sputtered with a uniform thin layer of Au of 14 nm thick, in a Bal-tec SCD 005 Sputter Coater (working distance: 50 mm, sputtering current: 30 mA, sputtering duration: 100 s). The Au-sputtered MPPC membranes were then used as the working electrodes in the electrodeposition process. The electrodepositing bath solution was 0.13 M $NiSO_4$, 0.13 M CH_3COONa and 0.1 M of Na_2SO_4 [21]. An anodic current density of 1.2 mA/cm^2 for durations from 0.5 h to 2.5 h was applied under continuous and vigorous stirring, and this resulted in a layered film comprising a dark, uniform layer of NHO on top of the Au-sputtered MPPC membrane. The as-deposited NHO made using this protocol was in the oxidized state, with an XRD profile shown as the black curves in Fig. 2B(a,b).

To fabricate folding structures with active crease patterns as shown in Figs. 4 and 5, a pre-designed Au pattern instead of a uniform layer had to be sputtered on the MPPC membranes. For the Miura and Yoshimura patterns shown in Fig. 5 and fig. S5, the corresponding Au patterns were achieved by placing inverse masks on top of the membranes before Au sputtering. The masks were designed by AutoCAD and fabricated by laser cutting acrylic plastic sheets of 2 mm thick. Crease patterns of NHO could then be electrodeposited on the membranes as shown in Fig. 4A(b), by the above bath electrodeposition protocol for 2 h. For the electrochemically stimulated Miura folds, to further increase the adhesion between NHO and the Au-sputtered membrane, an extra Au layer was electrodeposited on the Au-sputtered membrane before NHO electrodeposition. The Au electrodepositing bath solution was Oromerse SO Part B and 1.7M Na_2SO_3 with the volume ratio of 1:9. A cathodic current density of -0.1 mA/cm^2 for a duration of 30 min was applied without stirring, and this resulted in a uniform Au layer. The finger design comprising two actuating hinges for independent light stimulation in Fig. 6D and F was also

fabricated by inverse masks to leave two unpainted rectangular windows of 4 mm width by 8 mm length, which were then electrodeposited with NHO using an applied current density of 1.2 mA/cm^2 for 2 h.

For the Miura structure shown in Fig. 4A and 5, after the electrodeposition of the NHO crease pattern, the MPPC membrane was folded along the sharp creases manually to allow the device to actuate in the intended way when stimulated by light. To make the individual actuating creases shown in Fig. 1B(i), designated areas of the Au-sputtered MPPC membranes (8 mm width by 16 mm length) were painted with a marker pen to leave an unpainted rectangular area of 4 mm width by 8 mm length, onto which NHO was coated by subsequent bath-electrodeposition with an applied current density of 1.2 mA/cm^2 for 2 h.

The actuation characterization tests shown in figs. S2 and S3 were performed on cantilever actuators with NHO electrodeposited by the above bath electrodeposition protocol on uniformly Au-sputtered MPPC membranes. Part of the Au was adhered to Cu tape for electrical connection to the electrochemical workstation. The just fabricated actuators were cut into rectangular strips measuring approximately 15 mm by 3 mm to form the cantilever actuators.

Electrodeposition of Ni(OH)$_2$/NiOOH (NHO) and MnO$_x$ patterns on micro-porous polycarbonate (MPPC) membranes by microfluidic electrochemical writing

In the electrochemically triggered micro-finger shown in Fig. 6A to C, muscle groups of the NHO material were printed onto isolated Au areas, which were then individually connected to the workstation electrodes. To start with, the conductive Au areas were patterned by sputtering MPPC membranes covered with acrylic masks. Then, NHO was directly written onto the sputtered Au areas by the microfluidic electrochemical writing method discussed in Section 2.2, in which the required electrolyte was delivered locally by micro-fluidic means [33] (Figs. 1C(i) and 4B). An electrolyte containing 0.6 M NiSO$_4$, 0.53 M CH$_3$COONa and 0.1 M of Na$_2$SO$_4$ was put into the

syringe of the setup which has a capacity of 3 mL. The NHO was electrodeposited under a constant potential of 2.05 V applied to the Au areas of the membrane against the stainless-steel syringe needle. The inner diameter of the needle was 0.51 mm, and the printing was performed by moving the syringe needle at a speed of 50 mm/min. To achieve thicker active layers of NHO, the writing was conducted by repeatedly scanning over the same area for a total duration of 20 min. Each actuating layer measured 10 mm in length and was printed parallel to the folding hinge.

For the MnO_x printing, active MnO_x hinges were electrodeposited on Au sputtered areas pre-patterned by reversed acrylic masks. The MnO_x printing electrolyte was a mixture of 0.1 M $C_4H_6MnO_4 \cdot 4H_2O$ and 0.1 M Na_2SO_4 [52]. The constant potential and needle speed used for the writing were 2.3 V and 0.5 mm/min, respectively. The single curling actuator shown in fig. S4Bwas 5 mm wide, and it comprised eight parallel MnO_x actuating strips. Each actuating strip measured 5 mm in length and 1 mm in width, and was separated 2 mm apart. For the full micro-robotic hand shown in fig. S4A and Movie S1, each MnO_x active strip was 5 mm long and was printed for a total duration of 10 min.

Physical characterization

Scanning electron microscope (SEM) images were obtained with a LEO 1530 field-emission microscope to image the surface morphology and thickness of NHO. The thickness of the MPPC membranes was measured by Bruker DektakXT® stylus profiler. Microstructural characterization was carried out by in-plane grazing incidence X-ray diffraction (GIXRD). In-plane GIXRD was performed in a Rigaku SmartLab diffractometer with a fixed incidence angle of 0.5° using a monochromatic Cu K-alpha source (wavelength = 1.54 Å) with the scan rate being 1°/min at steps of 0.1°. For *in situ* XRD measurements, a lower scan rate of 0.05°/min was used. Transmission electron microscopy (TEM) imaging and selected area electron diffraction (SAED) were

performed in a FEI Tecnai G2 20 Scanning TEM. The Young's moduli of MPPC and NHO were measured by nanoindentation (Agilent Nano Indenter G200).

Light stimulated actuation tests

The light stimulated origami tests were performed with the NHO in the as-fabricated, oxidized state at ambient conditions in the laboratory, with temperature and RH being 24°C and 65%, respectively. An LED light source of nominal power rating of 30 W was utilized to trigger the actuation as shown in fig. S5A. By modifying the distance between the light source and the illuminated targeted area, the light intensities at the latter were varied from 30 to 150 mW/cm^2, as measured by a TES11333 solar power meter (TES Electrical electronic Corp.). The Miura lift was stimulated at light intensity ~120 mW/cm^2, with a load ~250 mg. For the independently controlled tests under light stimulation (Fig. 6D), two light sources combined with optical fibers were used to stimulate the actuating hinges. The light intensity at the hinges was around 30 mW/cm^2, as measured by a solar power meter.

Electro-chemical actuation tests

The electrochemical actuation tests in Figs. 1B, 3, 5 and 6 were carried out with the NHO in the as-fabricated, oxidized state, and the actuators were submerged into an electrolyte of 1 M NaOH solution in a rectangular glass container. One end of the actuator was fixed and connected to an electrochemical workstation (LK2006A, Lanlike or Corrtest, CS350) as the working electrode. In Fig 3 and figs. S2 and S3, the actuation was electrochemically induced by the cyclic voltammetry mode of the workstation from 0 V to 0.8 V with respect to an Ag/AgCl reference electrode in a 3-electrode cell setup with a platinum mesh counter electrode. The actuation motion was video-recorded and was further processed and analyzed by a motion tracking software Kinovea. The actuation performance of the printed fingers was characterized by fixing them vertically in the same three-electrode setup (Fig. 6A). Each muscle group was connected to a toggle switch which

enabled the actuator to switch between input voltage of 0.0 V and 0.8 V. For the Miura device, the freshly prepared actuator was fixed in 1M NaOH solution, with the reduced potential (-0.2 V) to actuate the Miura fold and oxidized potential (0.8 V) to recover it. Also, the actuator was stimulated by the potential window -0.1 V to 0.5 V with a scan rate of 3 mV/s to demonstrate the actuating performance vs varying potentials in quasi-equilibrium conditions. The Miura lift was stimulated by a step potential (-1 V) to lift a load ~120 mg in the 1M NaOH solution, where buoyancy was calculated as volume of the load times its density. The printed MnO_x curling actuator and the full hand were submerged in an electrolyte of 0.5 M Na_2SO_4 electrolyte in a rectangular glass container. The curling actuator was connected to a multiple toggle switch, enabling the input voltage to switch between different step potentials (see Section S2). For the printed MnO_x full hand, each finger was independently connected to a toggle switch, enabling the input voltage to switch between 0.0 and 1.0 V [23] relative to Ag/AgCl electrode, to actuate and recover each finger independently.

Data availability

All data needed to support the conclusions of this manuscript are included in the main text or the Supplementary Materials.

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Acknowledgments

Figures and Tables

A Ni(OH)$_2$/NiOOH actuating material (NHO)

Turbostratic crystal   Water molecule

$\beta - \text{Ni(OH)}_2$ →Oxidation→ ←Reduction← $\beta - \text{NiOOH}$

Larger   Smaller

Larger   Smaller

hv hv off

(i) Electrochemical actuation   (ii) Light actuation
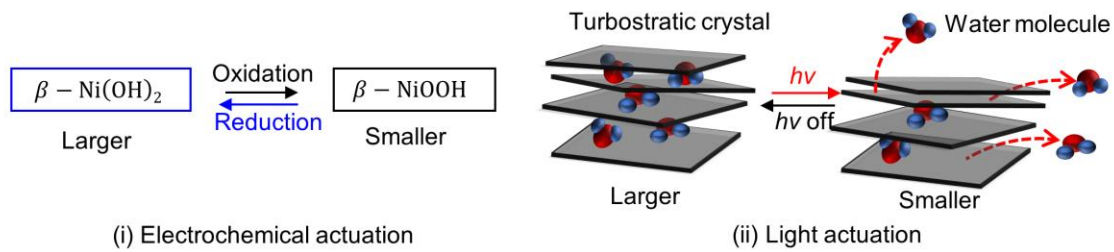
B "Minimalist" Origami design by deploying NHO as stimuli-response creases

NHO   Air hv on ... off

MPPC   Oxidized potential ... Reduced potential   Liquid

Light intensity (mW/cm^2)

Bending angle (°)

- Light stimulated actuation
- Electrochemically stimulated actuation

Potential (V vs Ag/AgCl)

(i) Stimuli-response crease

Reduction / Oxidation

(ii) Electrochemical actuation hv / hv off   (iii) Light actuation

C Enabling technologies

Conductive syringe needle delivering electrolyte

Potentiostat   Air   NiSO$_4$ − CH$_3$COONa − Na$_2$SO$_4$ electrolyte

Sputtered Au   NHO pattern

Moving MPPC substrate

(i) Microfluidic electrochemical writing of NHO

Top-view   Side-view   Interlock

Peeled off NHO

Interlocks left on the MPPC

Au sputtered MPPC substrate

(ii) Micro-riveting of NHO onto MPPC substrate

Fig. 1. "Minimalist" origami with stimuli-responsive creases. (A) The Ni(OH)$_2$/NiOOH (NHO)

material mixture exhibits reversible volume shrinkage on (i) oxidation, or (ii) upon visible light

illumination. **(B)** (i) Stimuli-responsive crease made by coating a 4mm-wide NHO strip (black)

onto micro-porous polycarbonate (MPPC) substrate (gray), under visible light stimuli of different intensities, and electrochemical stimuli at potential scan rate 25 mV/s relative to Ag/AgCl electrode in 1M NaOH electrolyte (see Movie S3). (ii, iii) Typical self-actuating Miura origamis with NHO crease patterns (dark colored) on MPPC membrane (gray colored) as origami substrate, under (ii) electrochemical actuation in 1M NaOH, and (iii) visible light actuation at intensity of 120 mW/cm^2. Scale bar: 10 mm. See Movie S3. **(C)** Enabling technologies to apply NHO to make self-folding origami creases: (i) microfluidic electrochemical writing of NHO onto origami substrate, and (ii) micro-riveting NHO onto MPPC membrane which serves as origami substrate. Insets in (ii) show SEM images of the (I) surface morphology and (II) cross-section view of NHO, and (III, IV) micro-rivets formed during electrodeposition. Scale bar: 2 μm.
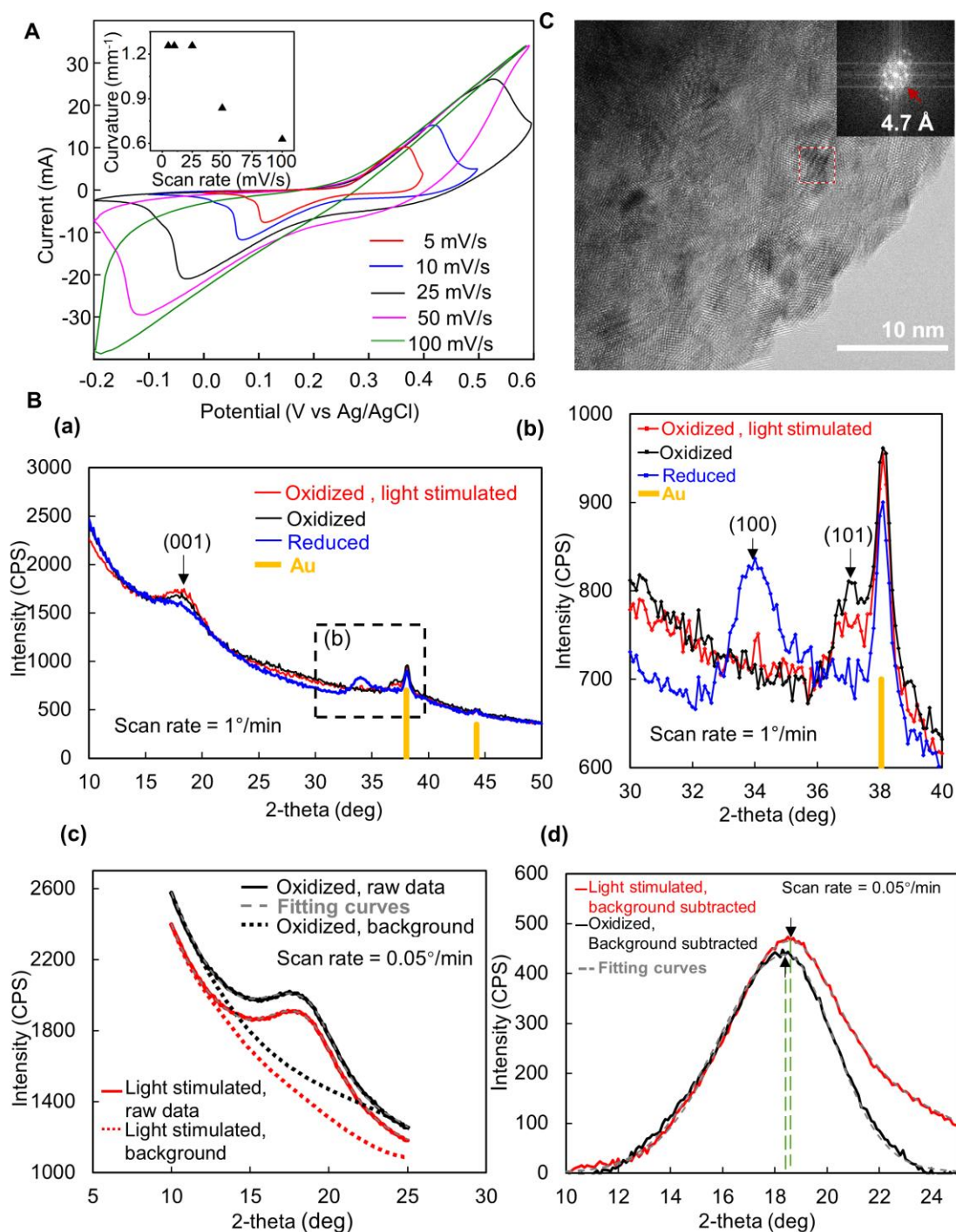
Fig. 2. Stimuli-responsive microstructural changes in NHO. (**A**) Cyclic voltammogram of NHO in 1 M NaOH at different scan rates; inset shows curvature at different scan rates. (**B**) (a) *In situ* GIXRD results of NHO under light stimulated oxidized (red), oxidized (black), and reduced (blue) states at scan rate of 1°/min. (b) Enlarged view of (a). (c) *In situ* GIXRD results of NHO

1 under light stimulated oxidized (red) and oxidized (black) at slower scan rate of 0.05°/min. (d)

2 Background subtracted XRD spectra of (c). (**C**) HRTEM micrograph of oxidized NHO.
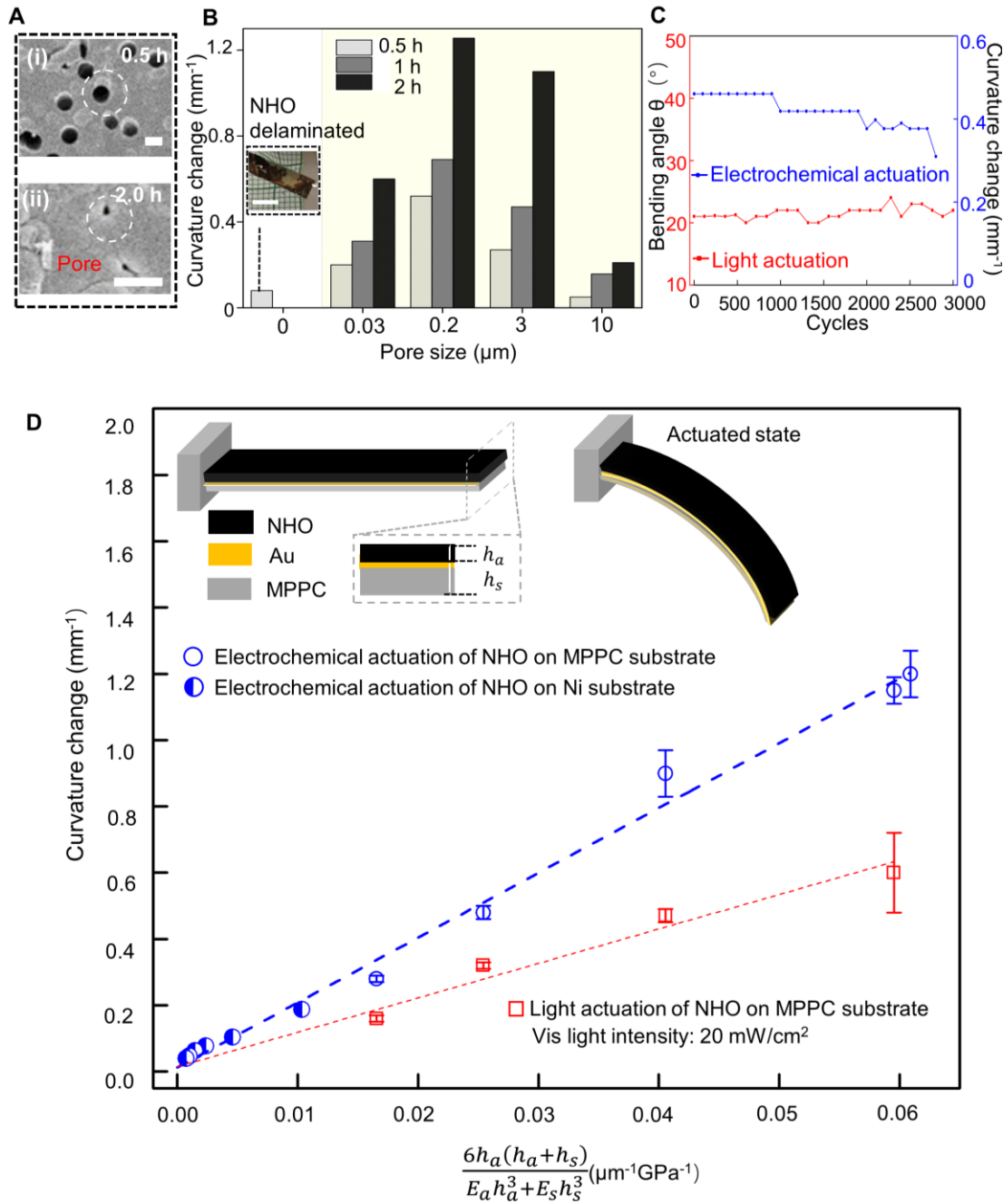
3

4 **Fig. 3. Enabling technology: substrate/interface engineering.** (**A**) SEM images showing the

5 pores filling process at (i) 0.5 h and ii) 2 h during electrodeposition of NHO. Scale bar: 2 μm. (**B**)

6 Effect of pore sizes of MPPC on the actuation performance and structural integrity; inset: an

7 actuator made by electrodepositing NHO on a non-porous PC membrane substrate for 0.5 h with

8 significant delamination just after 5 cycles, scale bar: 5 mm. (**C**) Device bending angle change

over 3000 cycles. The electrochemical actuation test was performed under step potential from 1 V

for 1 s to -1 V for 1 s in 1 M NaOH; the light actuating was performed under the light intensity of

~20mW/cm². (**D**) Bending curvature change κ vs $\dfrac{6h_a(h_a+h_s)}{E_a h_a^3 + E_s h_s^3}$ for NHO electrodeposited on

MPPC and on Ni substrates [*21*] under electrochemical actuation in 1 M NaOH electrolyte, and

light actuation under visible light of around 20 mW/cm². Inset: schematic diagram of an actuator

at recovered and actuated state.
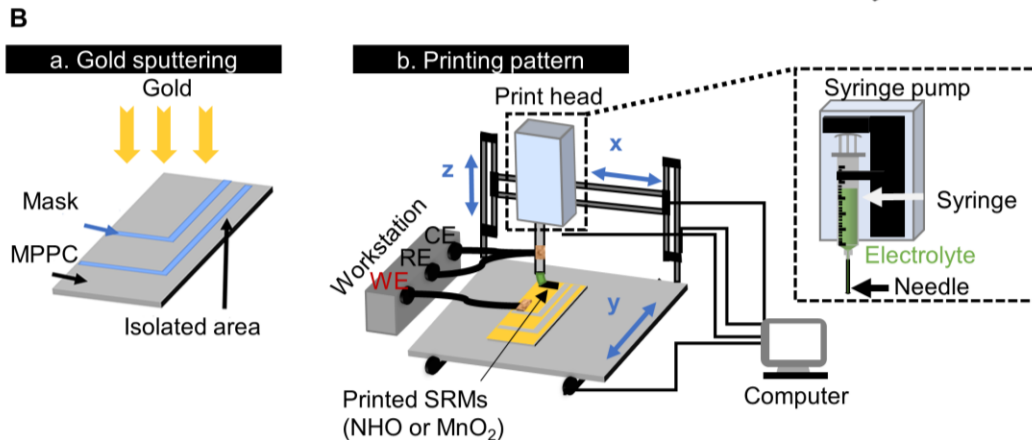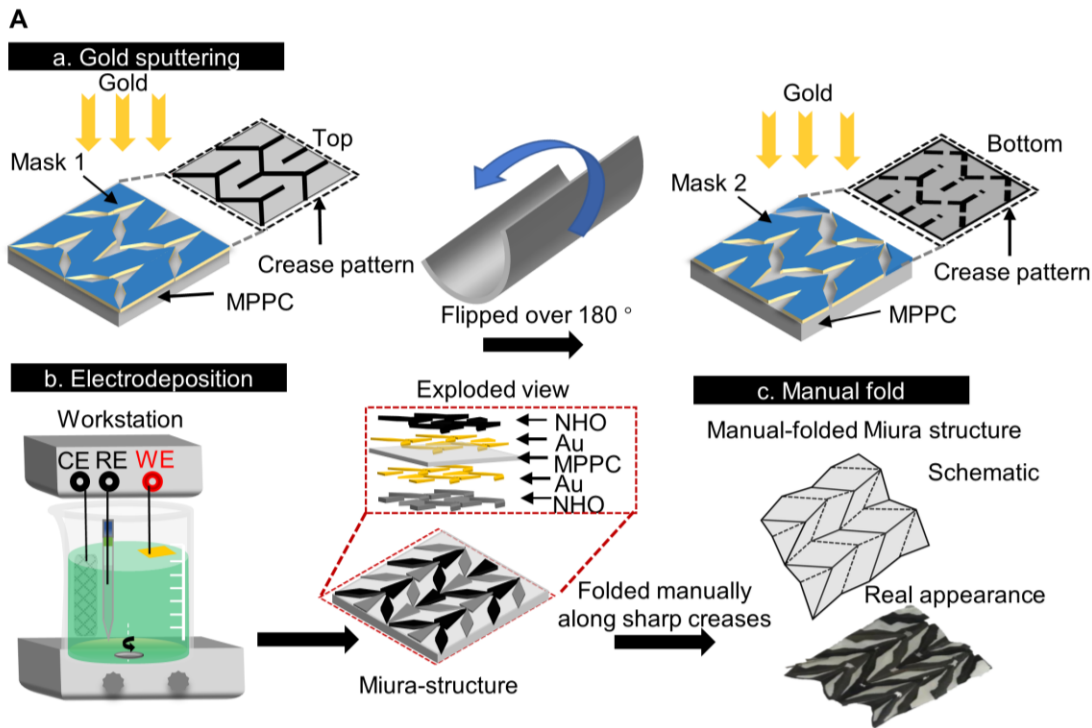
Fig. 4. Enabling technology: Pattern fabrication of SRM. (**A**) Two-sided, mask-based bath-

electrodeposition. (**B**) Direct SRM pattern printing on Au-sputtered areas of MPPC membranes

by a microfluidic electrochemical writing method.
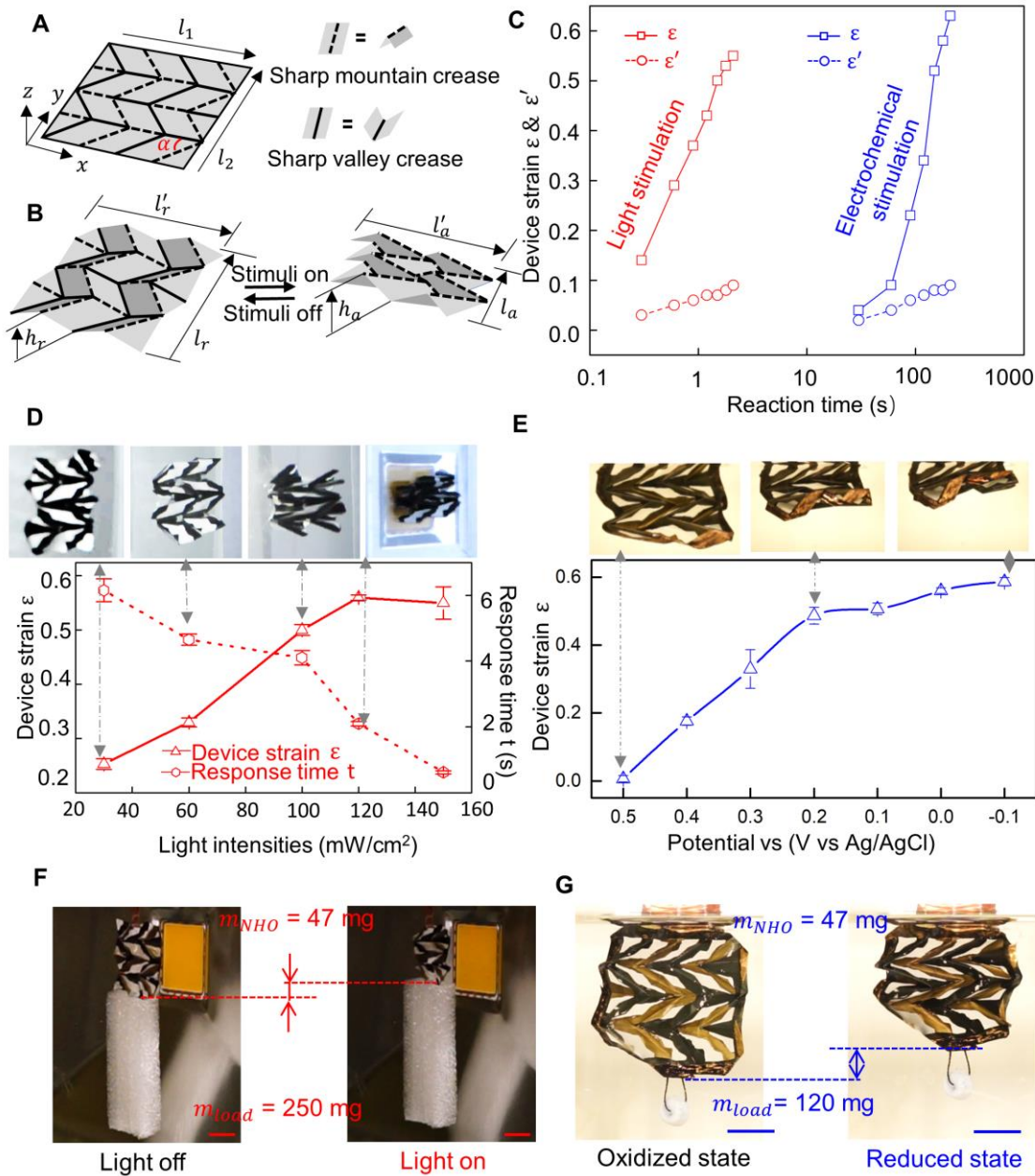
Fig. 5. Light (red) and voltage (blue) triggered actuation of self-actuating Miura structure

based on sharp NHO creases. (A-B) Schematic of Miura fold. (A) Sharp-crease design for the

Miura structure, with dashed line for sharp mountain creases and solid line for sharp valley

creases. (**B**) Schematic Miura fold at recovered (stimuli off) and actuated (stimuli on) states.

Widths l_r and l_a in the recovered and actuated states, respectively, define the device strain ε

along the l_2 direction according to $\varepsilon = (l_r - l_a)/l_r$. Device strain ε' perpendicular to the l_2 direction is defined as $\varepsilon' = (l'_r - l'_a)/l'_r$. **(C)** Experimental device strains ε and ε' along and perpendicular to the l_2 direction, respectively, vs time, under light stimulation at ~120 mW/cm^2 intensity (red), and electrochemical stimulation with potential -0.2 V applied relative to Ag/AgCl electrode in 1M NaOH electrolyte (blue). Time zero refers to the moment the stimulation was switched on. **(D)** Device strain ε along l_2 and response time of Miura micro-robot at different light intensities from 30 mW/cm^2 to 150 mW/cm^2. **(E)** Device strain ε along l_2 direction in response to varying potential from 0.5 V (oxidized state) to -0.1V (reduced state) with a slow scan rate of -3mV/s to maintain quasi equilibrium at each potential value. **(F, G)** Miura lift: **(F)** under light stimulation at 120 mW/cm^2 intensity (load: 250 mg), see Movie S7 for details; **(G)** under electrochemical stimulation by potential -1 V relative to Ag/AgCl electrode in 1M NaOH electrolyte (load: ~120 mg after accounting for buoyancy). See Movie S8 for details.
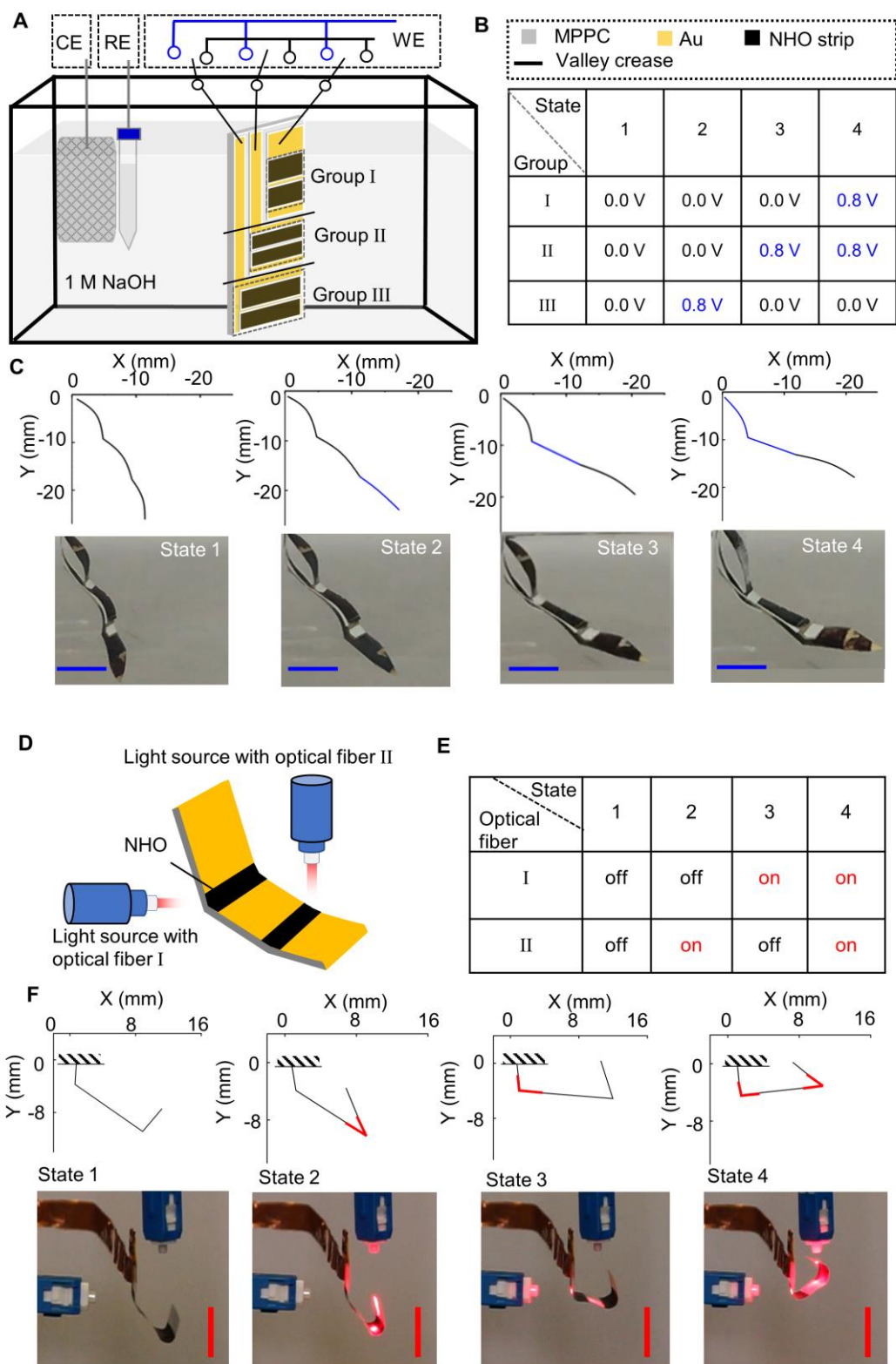
Fig. 6. **Electrochemically and light triggered micro-robotic fingers with independently controlled muscle groups. (A~C)** Electrochemically stimulated finger. **(A)** Schematic diagram and actuation set-up of the printed finger comprising three independently controlled muscles. **(B)**

Exemplary control states of voltage signals (values in volts). **(C)** Actual motion of the robotic

finger with NHO muscles under the four exemplary states illustrated in **(B)**, scale bar: 10 mm, and

see Movie S9 for details. **(D~F)** Locally light stimulated finger. **(D)** Schematic diagram and

actuation set-up of finger comprising two independently controlled hinges stimulated locally by

two light sources with optical fibers at light intensity ~30 mW/cm^2. **(E)** Exemplary control states

of light signals. **(F)** Actual motion of robotic finger with NHO hinges under the four exemplary

states illustrated in **(E)**, scale bar: 10 mm, see Movie S10 for details.

Additional information

Section S1. Intrinsic actuation stress from bending curvature

Section S2. Electrochemical actuation

Section S3. Light actuation

Fig. S1. The schematic diagrams of a bi-layered actuator.

Fig. S2. Actuating performance of NHO under different fabrication conditions.

Fig. S3. The best performing electrochemical NHO actuator.

Fig. S4. Electrochemically triggered micro-robots made by printed MnO$_x$.

Fig. S5. Light actuation test setup.

Fig. S6. Cathodic current peak and curvature at different scan rate.

Fig. S7. Curvature at scan rate ranging from 25 mV/s to 250 mV/s.

Fig. S8. Bending angle of single origami crease hinge over 1000 cycles.

Table S1: A summary of origami actuators fabricated by stimuli-responsive materials.

Movie S1. A robotic hand with independently printed and controlled MnO$_x$ finger hinges,

stimulated in 0.5 M Na$_2$SO$_4$, with each finger under step potential 0 V to actuate and 1 V to

recover. (Play speed: ×2)

Movie S2. Actuating performance of the NHO cantilever actuator in 1 M NaOH solution cyclic with a scan rate of 25 mV/s with potential window of 0.8 V. (Play speed: ×5)

Movie S3. Single smooth NHO fold in response to light (play speed: ×3) and electrochemical stimulations. (Play speed: ×8)

Movie S4. Light stimulated Miura fold based on NHO creases. (Play speed: ×1)

Movie S5. Fast response and light stimulated Miura fold based on NHO creases under light intensity 150 mW/cm^2. (Play speed: ×1)

Movie S6. Electrochemically stimulated Miura fold based on NHO creases with step potential (-0.2 V) to actuate and (0.8 V) to recover. (Play speed: ×25)

Movie S7. Light stimulated Miura structure based on NHO creases lifts a load (~250 mg) under light intensity of 120 mW/cm^2. (Actuating process: play speed: ×1; relaxing process: play speed ×5)

Movie S8. Electrochemically stimulated Miura structure based on NHO creases lifts a load (~120 mg after accounting for buoyancy) with step potential (-1 V). (Play speed: ×25)

Movie S9. Printed actuator with three independently controlled NHO muscles groups, mimicking the finger movements. (Play speed ×4)

Movie S10. Finger geometry with two independently local controlled NHO hinges stimulated locally by light. (Actuating process: play speed: ×1; recovering process: play speed × 2)

Movie S11. The curling actuating performance of printed MnO$_x$ actuator in 0.5 M Na$_2$SO$_4$ under different step-potential stimulations. (Play speed: ×2)

Movie S12. Smooth NHO Yoshimura unit fold under various light intensities. (Play speed: ×5)

SUPPLEMENTARY MATERIALS

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Section S2. Electrochemical actuation

Section S3. Light actuation

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Supplementary Materials

Section S1. Intrinsic actuation stress from bending curvature

Here, the intrinsic actuating stress characteristics of the active NHO material are analyzed by Timoshenko's theory [31]. The configuration analyzed is shown in fig. S1, where an active actuating layer expands, causing the underneath passive layer to bend. The thin Au pre-sputtered layer is ignored since its nanometric thickness is negligible compared with the micron-scale h_a and h_s in the present experiments. As indicated in fig. S1B as the active layer attempts to expand with an actuation force $P = P_a$ per unit width, the resultant effect on the underlying passive layer is a tensile force of the same magnitude $P = P_s$. Therefore, the force couple P produces bending moments $M_a = E_a I_a \kappa$ and $M_s = E_s I_s \kappa$ in each of the two layers, so that $P(h_a + h_s)/2 = (E_a I_a + E_s I_s)\kappa$, where $I_a = h_a^3/12$ and $I_s = h_s^3/12$, E_a and E_s are Young's moduli of the active and substrate layers respectively, and κ is the bending curvature. The average actuation stress $\sigma_a = P/h_a$ exerted by the active layer is therefore

$$\kappa = \frac{6h_a(h_a + h_s)}{E_a h_a^3 + E_s h_s^3}\sigma_a \tag{S1}$$

In the active layer, a chemical, plastic strain ε_a^{chem} acts to cause the actuation, and this plays the role of the mismatch strain in Timoshenko's theory, i.e. when the actuating layer is freed out from the substrate, it will be longer than the substrate by strain ε_a^{chem} as shown in fig. S1C. Timoshenko gave this strain as:

$$\varepsilon_a^{chem} = \left[\frac{h_a + h_s}{2} + \frac{E_a h_a^3 + E_s h_s^3}{6(h_a + h_s)}\left(\frac{1}{E_a h_a} + \frac{1}{E_s h_s}\right)\right]\kappa = \left[\frac{1}{E_a} + \frac{h_a}{E_s h_s} + \frac{3h_a(h_a + h_s)^2}{E_a h_a^3 + E_s h_s^3}\right]\sigma_a \tag{S2}$$

The work density U of the actuating mechanism is $U = \int \sigma_a d\varepsilon_a^{chem}$, or, from Eq. (S2),

$$U = \frac{\sigma_a^2}{2}\left[\frac{1}{E_a} + \frac{h_a}{E_s h_s} + \frac{3h_a(h_a + h_s)^2}{E_a h_a^3 + E_s h_s^3}\right] \tag{S3}$$
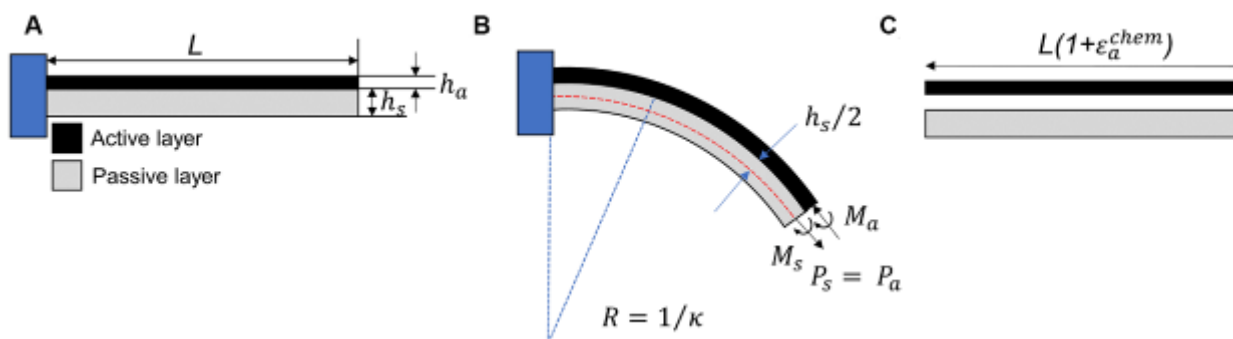
Fig. S1. The schematic diagrams of a bi-layered actuator (**A**) when the actuating layer is in the oxidized state; (**B**) when the actuating layer is in the reduced state; (**C**) if the actuating layer was freed from the substrate.

Section S2. Electrochemical actuation

To measure the intrinsic actuation stress of the NHO material under electrochemical stimulation, NHO films of different thicknesses h_a were fabricated on 10 µm thick (h_s) MPPC membranes by bath electrodeposition (see Materials and Methods). Electrochemical actuation tests were then carried out in 1 M NaOH electrolyte (see Materials and Methods). As shown in fig. S2A, the actuator exhibited large curling motion towards the membrane side when reduced (during negative potential scan) and straightened or even curled backward to the side of the active material when oxidized (during positive potential scan). This corresponds to the actuating layer expanding during reduction and contracting during oxidation. To optimize the electrodeposition conditions for NHO, the effects of the electrodeposition current density were first investigated. At an electrodepositing time of 0.5 h, fig. S2B shows direct linearity between the thickness of the electrodeposited NHO layer and the current density. The average bending angle of the first five actuation cycles first increases with the current density and then drops beyond 1.2 mA/cm^2, due likely to the poor adhesion of the NHO layer on the Au-sputtered MPPC membrane at the highest electrodepositing current density of 1.6 mA/cm^2, as evidenced by the occasional observation of the layer peeling off from the membrane. Therefore, the optimized current density is selected to

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be 1.2 mA/cm^2. Figure S2C shows the effect of the electrodepositing time at current density of 1.2

mA/cm^2, on the thickness of the NHO layer and also the subsequent actuation maximum

curvature. The results show that both the thickness of the actuating layer and the actuating

curvature first increase approximately proportionally with the electrodepositing time but then

saturate to steady values for the times larger than 2 h. The typical largest curvatures achieved over

the potential scan covering the redox regime at different electrodepositing times are shown in fig.

S2D.
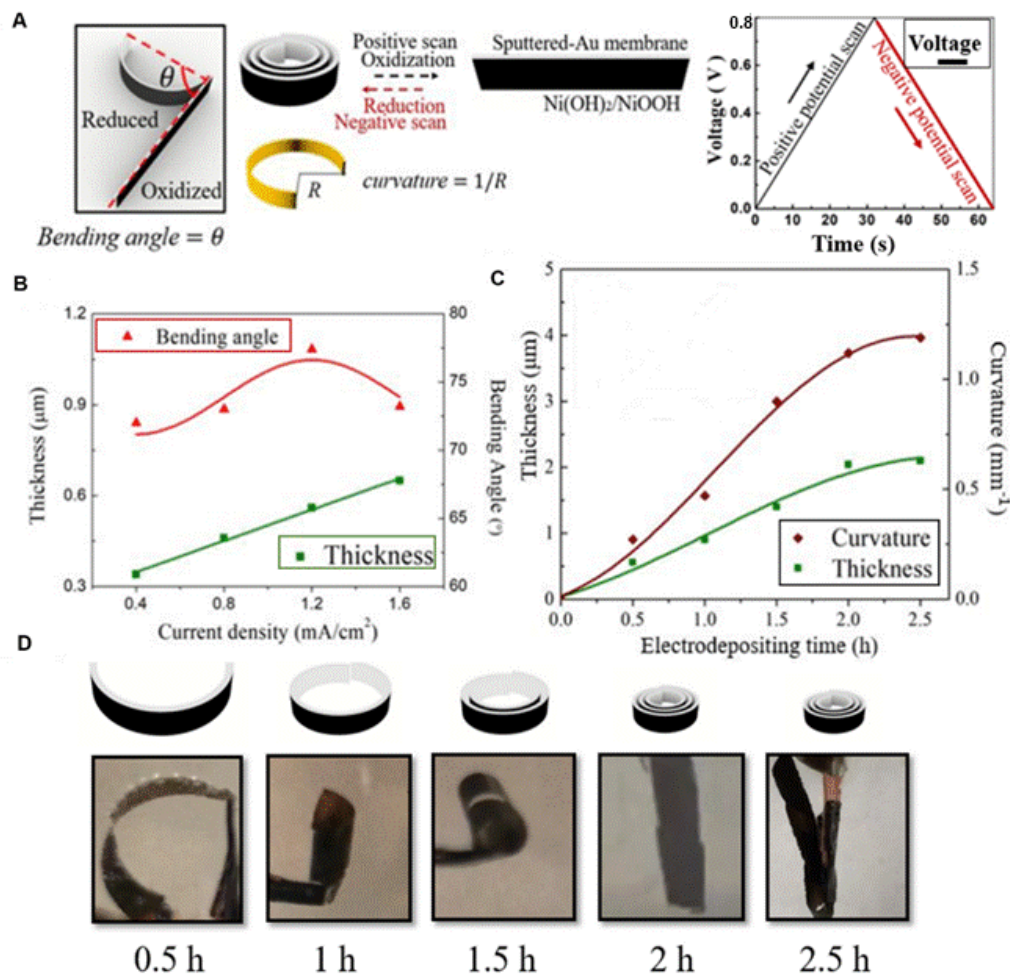
Fig. S2 Actuating performance of NHO under different fabrication conditions. (**A**) Schematic showing bending angle and curvature during negative and positive potential scan (the active material layer is drawn as black, while the substrate is white). (**B**) Effects of current density for 0.5 h on thickness of electrodeposited Ni(OH)$_2$/NiOOH layer and subsequent actuation

bending. (**C**) Effects of electrodepositing time on the typical largest curvature. (**D**) Typical largest curvature during electrodeposition time ranging from 0.5 h to 2.5 h.

The data in fig. S2C are replotted in Fig. 3D of the main text as curvature κ vs $\left[\dfrac{6h_a(h_a + h_s)}{E_a h_a^3 + E_s h_s^3}\right]$, according to the format suggested by Eq. (S1). Here, the h_s for the MPPC substrates is fixed at 10 µm, $E_s = 2.3$ GPa, $E_a = 24 \pm 5.6$ GPa by nanoindentation tests (see Materials and Methods), and h_a varies between 0.6 to 2.2 µm. As mentioned above, the Au layer deposited on top of the MPPC membrane is ignored since it is very thin at just 14 nm (see Materials and Methods). In addition, data from an earlier report [21] for NHO on Ni substrates are also plotted, where the NHO thickness was constant at 0.44 µm, the Ni substrate thickness h_s varied from 1.2 to 5.5 µm, and $E_s = 220$ GPa for Ni. The original device strains (*D/L*) reported in [21], where *D* is end-deflection of the cantilever actuators of length *L*, are converted into bending curvature κ by using the geometrical relation $\kappa = 2(D/L)/\left\{L\left[1 + (D/L)^2\right]\right\}$ which gives sufficient accuracy for the range studied. The plot indicates that Eq. (S1) is obeyed for both the current NHO-on-MPPC actuators as well as the previous NHO-on-Ni ones, with a fairly constant σ_a of 20 MPa. It is also intriguing to see that the NHO material is delivering such a constant intrinsic actuating stress over a large curvature range, from nearly zero to about 1.2 mm^{-1}. The actuating stress of ~20 MPa here is large among electrochemical actuators [40].

Best electrochemical actuation performance – In Fig. 3D of the main text, the largest actuation curvature achieved in the present work is 1.2 mm^{-1}, with the NHO layer electrodeposited for 2 h (fig. S2C). Figure S3 and Movie S2 show the typical actuation of this actuator, of size measuring 15 mm × 3 mm. During the negative potential scan in the latter half of the potential cycle, the curvature increased rapidly after ~0.4 V, due to the reduction reaction of NiOOH into Ni(OH)$_2$, leading to large expansion of the active layer. The actuator also exhibited a slight twisting motion, possibly due to the slightly uneven deposition of the actuating material. At

the end of the negative scan, the actuator underwent a cumulative angular deflection of >1000°

(i.e. 2.8 revolutions) at the free-end, and from this, the curvature is estimated at 1.2 mm^{-1}. The

actuation strain ε_a^{chem} calculated from Eq. (S2) is 1%, and the work density calculated from Eq.

(S3) is $U = 97$ kJ/m^3.

Therefore, in summary, the present NHO material can deliver a constant actuating stress of

19.5 ± 0.5 MPa over strains up to 1%, and work density up to ~100 kJ/m^3. The maximum work

density here already outperforms human skeletal muscles (~40 kJ/m^3) [32] and is comparable to

that of typical metallic muscles [53]. Although it is smaller than ferroelectric polymers actuators

(~1 MJ/m^3) [32] and the best nanoporous noble alloys (~6 MJ/m^3) [54], the NHO material is a lot

cheaper than nanoporous noble metals, and the triggering voltage needed is under 1 volt, which is

much lower than that of ferroelectric polymers (typically >1 kV). The actuating stress of ~20 MPa

here should be an intrinsic property of the NHO material at room temperature, but the maximum

strain and work density are only for the present actuator configurations. From Eq. (S1), the

curvature should further increase by increasing the thickness of the active layer, or decreasing the

stiffness of the substrate. However, the maximum thickness of the NHO layer that can be

achieved by the present fabrication method is about 2 µm even after prolonged electrodeposition

(fig. S2C), and this is already the case for the best performing actuator shown in fig. S3.

Therefore, further increase in actuation can only be achieved by using even softer or thinner

substrates. As the unit cell volume of Ni(OH)$_2$ is known to contract by approximately 10% when

it is oxidized into NiOOH [29, 55] further improvements of the actuating strain are highly

possible by using more compliant substrates.
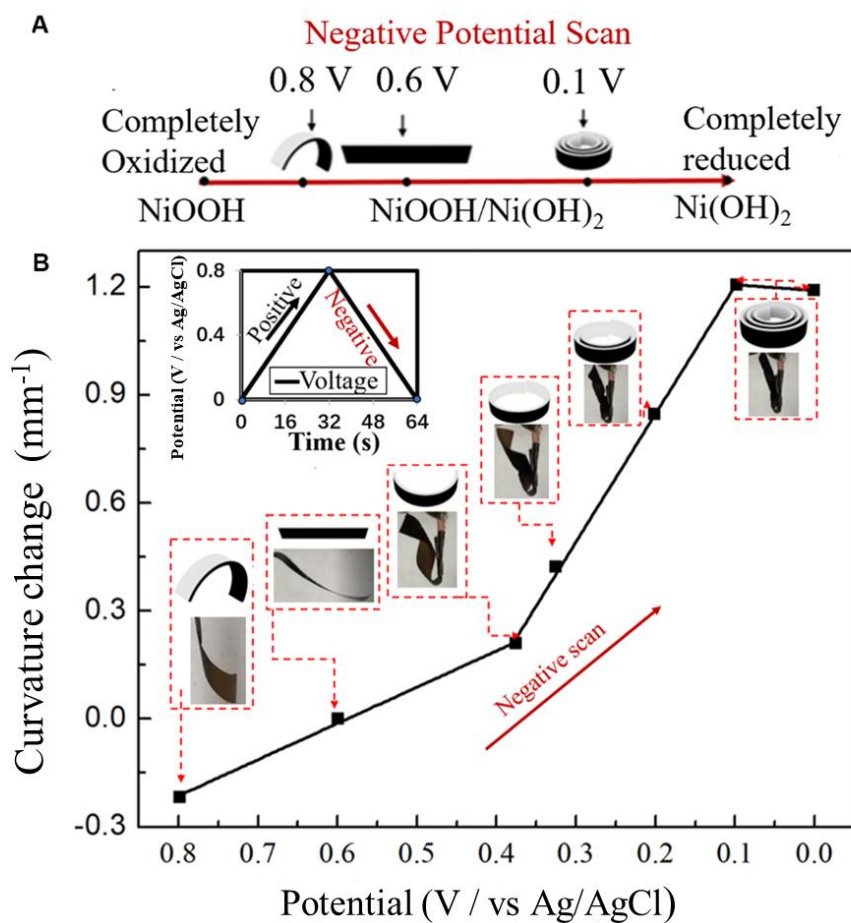
Fig. S3. The best performing electrochemical NHO actuator. (**A**) Curvature change trend from oxidized state to reduced state (half reduced cycle). (**B**) Curvature change during negative scan (half reduced cycle) from 0.8 V to 0 V at 25 mV/s. See Movie S2 for details.

To demonstrate the wide applicability of the two technical advancements discussed in the Section 2, another proven electrochemically stimulated material MnO_x [23] was also used to make actuating creases with the same micro-fluidic electrochemical printing and micro-riveting strategies (see Fig. 4B, and Materials and Methods). The printed actuating patterns of MnO_x demonstrate good adhesion with the porous polymeric substrate, thus proving the versatility of the micro-riveting and the microfluidic printing strategies. Results show that, by printing several parallel MnO_x actuating strips on the polymeric substrate, the printed actuator was able to demonstrate large curling motion during the redox reaction, as shown in fig. S4. For the same curling actuator, by applying different step potentials, the curling speed can be modified. By

1 comparing the same curling range, the curling speeds for different step-potential changes are:

2 ~12 deg/s from 1V to 0.3 V, 19 deg/s from 1 V to 0.2 V, and 30 deg/s from 1 V to -0.5 V. Fig.

3 S4B and Movie S11 show the fast response achieved by step potentials of 1 V to recover and -0.5
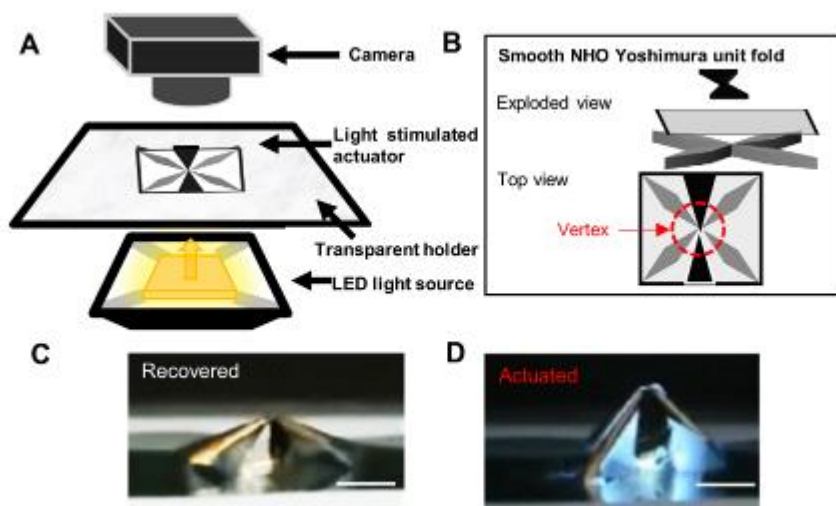
4 V to actuate.
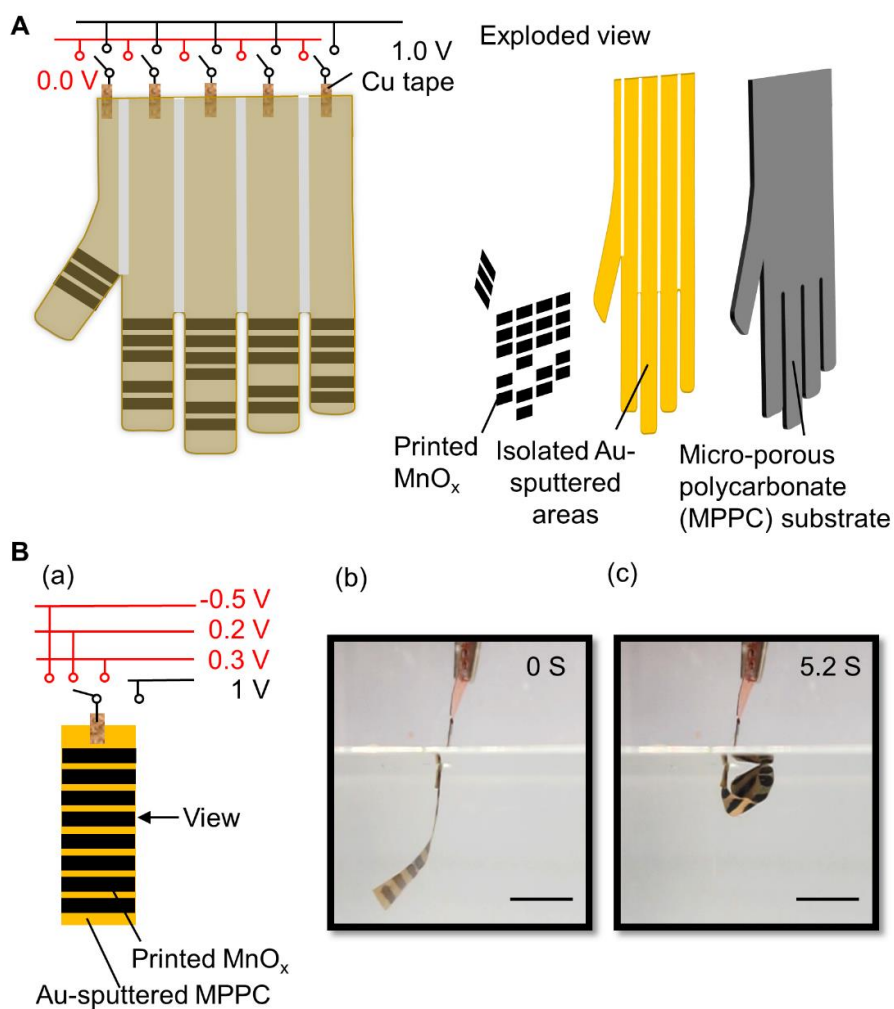
Fig. S4. Electrochemically triggered micro-robots made by printed MnO$_x$. (A) Schematic diagram of the printed MnO$_x$ full hand comprising five independenlty controlled fingers. **(B)** Curling actuator. (a) Schematic diagram of the printed MnO$_x$ curling actuator. (b) Recovered state under step potential of 1 V relative to Ag/AgCl electrode in 0.5 M Na$_2$SO$_4$. (c) Actuated state under step potential of -0.5 V relative to the same electrode and in the same electrolyte. Scale bar: 5 mm.

Section S3. Light actuation

To determine the typical σ_a of the NHO material on light stimulation, NHO films of various thicknesses h_a from 0.6 to 2.1 µm were bath-electrodeposited on MPPC membranes with $h_s = 10$ µm at an optimized current density of ~1.2 mA/cm^2 (see Materials and Methods). Light stimulation tests were carried out on the actuators (15 mm × 3 mm) under a visible light intensity of ~20 mW/cm^2. The actuators exhibited curling motion towards the NHO side in response to the light illumination, and started to straighten back to the side of the membrane when the light source was removed. This corresponds to the actuating layer contracting due to water desorption [*22*] under light illumination, and recovery due to water absorption [*22*] when the light is turned off. The curvature κ data are also plotted in Fig. 3D (in red) of the main text vs the factor $\left[\dfrac{6h_a(h_a + h_s)}{E_a h_a^3 + E_s h_s^3} \right]$. Linearity is observed as in agreement with Eq. (S1), and the slope indicates a value of 10.8 MPa for σ_a under ~20 mW/cm^2 visible light illumination. The largest actuation curvature change is 0.6 mm^{-1} for the thickest NHO layer of 2.1 µm tested. The corresponding light stimulated actuation strain is 0.5% as calculated by Eq. (S2), with the work density being 28 kJ/m^3 from Eq. (S3). Therefore, under visible light illumination at ~20 mW/cm^2, the present NHO material can deliver a constant actuating stress of ~11 MPa, with strains up to ~0.5% and work density up to 28 kJ/m^3.

Light actuation test setup – Light stimulation experiments in Figs. 1B, 3 and 5 of main text were carried out using a setup illustrated in fig. S5A (see Methods for details). Figures S5C and D show the application to the example of a Yoshimura origami unit [*51*] involving two smooth NHO valley creases (black) and four mountain creases (gray) (fig. S5B).Under light illumination at 40 mW/cm^2, the actuator underwent self-folding in around 10 seconds as shown in fig. S5C and D, and at a higher light intensity of 100 mW/cm^2, the self-folding process could be completed much quicker in around 4 seconds (see Movie S12).

Fig. S5. Light actuation test setup. (**A**) Schematic of light stimulation of origami actuators. (**B**) Schematic of Yoshimura unit comprising smooth NHO valley and mountain creases. (**C** and **D**) Light stimulated response of an actual self-actuating Yoshimura unit at recovered (C) and actuated (D) states at light intensity of 40 mW/cm^2 (scale bar: 5 mm).
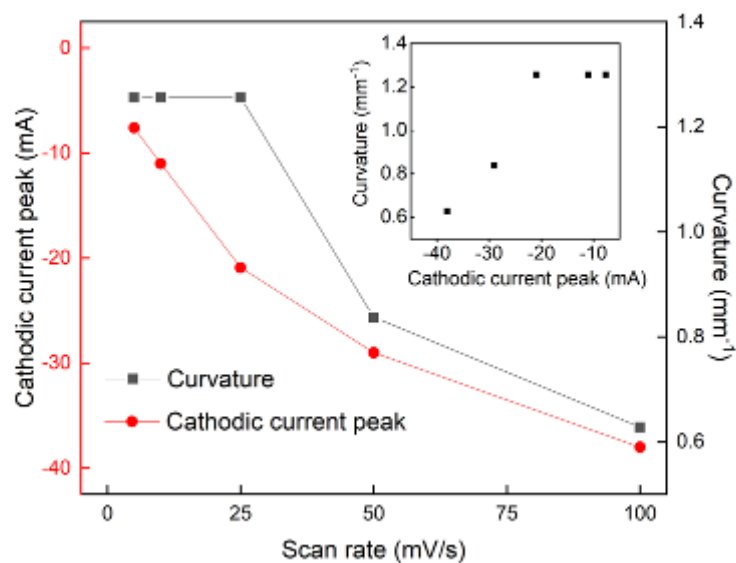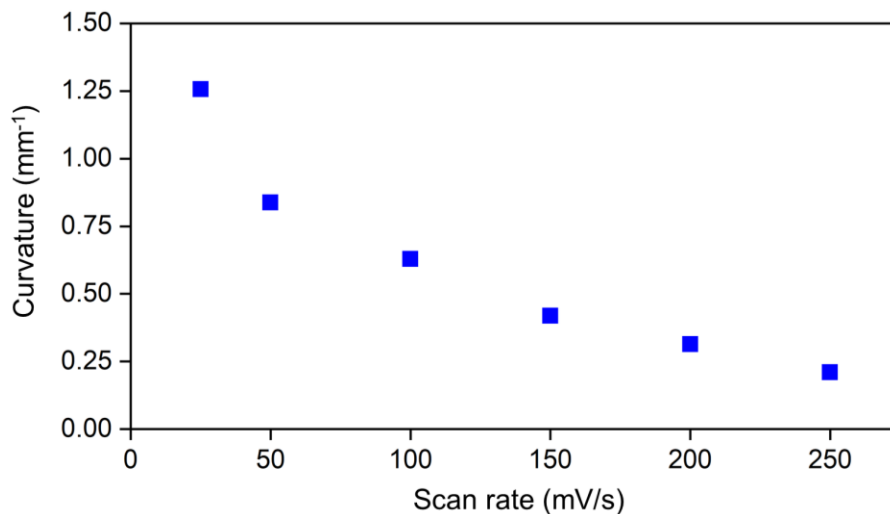
1

2 **Fig. S6. Cathodic current peak and curvature at different scan rate,** with the inset showing

3 the curvature vs the cathodic current peak.

4

5

6 **Fig. S7. Curvature at scan rate ranging from 25 mV/s to 250 mV/s.** A fixed potential range of

7 -0.2 V to 0.6 V was applied in 1 M NaOH electrolyte. The sample used here was the actuator that

8 was electrodeposited for two hours on the substrate with pore size of 0.2 μm.

9
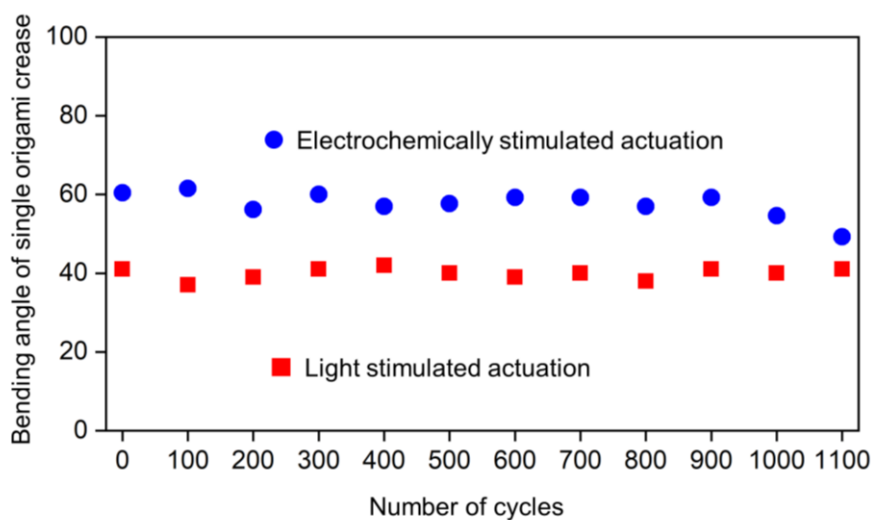
Fig. S8. Bending angle of single origami crease hinge over 1000 cycles, with a single crease triggered by step potential under -1 V for 0.5 s to actuate and 1 V for 1 s to recover in 1 M NaOH electrolyte and under illumination of vis light intensity at ~25 mW/cm^2 on for 0.5 s to actuate and 1 s off to recover for both 1000 times.

Table S1: A summary of origami actuators fabricated by stimuli-responsive materials.

Materials	Response time	Fabrication complexity and costs	Stimuli	Reference
Shape memory polymers	Slow in terms of hours	Easy and cheap	Water (recovered by acetone)	[13]
Shape memory polymers and hydrogels	Slow in terms of hours	Relatively complex but cheap	Water combined with temperature	[14]
Shape memory polymers	Slow in tens of minutes	Easy and cheap	Temperature	[15]
Temperature-sensitive hydrogels	Slow in terms of minutes	Relatively complex but cheap	Temperature	[16]
Liquid-crystal elastomers	Fast in terms of several seconds	Relatively complex requiring programming process but cheap	Temperature	[17]
shape memory polymer fibers	Slow in terms of minutes	Easy and cheap	Temperature	[18]
Graphene oxide and reduced graphene oxide	Fast in terms of seconds	Complex and expensive	NIR light	[20]
Transition metal hydroxides/oxides	Fast in terms of ~2 seconds for light stimulation; Slow in terms of a few to tens of minutes for electrochemical stimulation.	Easy and cheap	Low-intensity vis light (~1 sun) or mild electrochemical potential (< 1 V)	Present work

Movies S1 to S12

Movie S1. A robotic hand with independently printed and controlled MnO_x finger hinges, stimulated in 0.5 M Na_2SO_4, with each finger under step potential 0 V to actuate and 1 V to recover. (Play speed: ×2)

Movie S2. Actuating performance of the NHO cantilever actuator in 1 M NaOH solution cyclic with a scan rate of 25 mV/s with potential window of 0.8 V. (Play speed: ×5)

Movie S3. Single smooth NHO fold in response to light (play speed: ×3) and electrochemical stimulations. (Play speed: ×8)

Movie S4. Light stimulated Miura fold based on NHO creases. (Play speed: ×1)

Movie S5. Fast response and light stimulated Miura fold based on NHO creases under light intensity 150 mW/cm^2. (Play speed: ×1)

Movie S6. Electrochemically stimulated Miura fold based on NHO creases with step potential (-0.2 V) to actuate and (0.8 V) to recover. (Play speed: ×25)

Movie S7. Light stimulated Miura structure based on NHO creases lifts a load (~250 mg) under light intensity of 120 mW/cm^2. (Actuating process: play speed: ×1; relaxing process: play speed ×5)

Movie S8. Electrochemically stimulated Miura structure based on NHO creases lifts a load (~120 mg after accounting for buoyancy) with step potential (-1 V). (Play speed: ×25)

Movie S9. Printed actuator with three independently controlled NHO muscles groups, mimicking the finger movements. (Play speed ×4)

Movie S10. Finger geometry with two independently local controlled NHO hinges stimulated locally by light. (Actuating process: play speed: ×1; recovering process: play speed × 2)

Movie S11. The curling actuating performance of printed MnO_x actuator in 0.5 M Na_2SO_4 under different step-potential stimulations. (Play speed: ×2)

1   Movie S12. Smooth NHO Yoshimura unit fold under various light intensities. (Play speed: ×5)