

## High-frequency and rapid response tungsten sulfide nano onion-based electrochemical actuators

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### Theoretical Framework

#### *Electrochemical potential*

The stress-dependent electrochemical potential is:

$$\mu_{\sigma} = \frac{\partial \Psi}{\partial c} \quad (\text{S1})$$

where  $c$  is the concentration of guest ions. The concentration-dependent energy  $\Psi$  is:

$$\Psi = \frac{1}{2} \varepsilon^e : C : \varepsilon^e + \mu_0 c + RTc (\ln \hat{c} - 1) + \rho \varphi \quad (\text{S2})$$

where the first term after the equal sign represents elastic energy,  $\varepsilon^e$  is the elastic strain,  $C$  is the elasticity matrix. The second and the third terms after the equal sign represent the chemical free energy, where  $\mu_0$  is the reference chemical potential at the standard state, the normalized concentration  $\hat{c} = c / c_{\max}$ ,  $c_{\max}$  is the maximum concentration of the guest ions in electrolyte,  $R$  and  $T$  are gas constant and reference temperature, respectively. The fourth term after the equal sign represents the free charge-dependent electrostatic energy,  $\varphi$  is the electric potential and  $\rho$  is the bulk charge density:

$$\rho = zFc \quad (\text{S3})$$

where  $z$  is the number of effective charge and  $F$  is the Faraday constant.

Equation (S1) is then expressed as:

$$\frac{\partial \Psi}{\partial c} = \frac{\partial \varepsilon^e}{\partial c} : C : \varepsilon^e + \mu_0 + RT \ln \hat{c} + zF\varphi = \sigma_{ij} : \frac{\partial \varepsilon_{ij}^e}{\partial c} + \mu_0 + RT \ln \hat{c} + zF\varphi \quad (\text{S4})$$

The elastic strain can be obtained by subtracting the chemical process-induced strain from the total strain:

$$\varepsilon_{ij}^e = \varepsilon_{ij}^t - \varepsilon_{ij}^c = \varepsilon_{ij}^t - \frac{1}{3} \left( \Omega c + \lambda \int_0^t c dt \right) \delta_{ij} \quad (\text{S5})$$

where  $\lambda$  is the chemical reaction factor. Equation (S4) is therefore given by:

$$\begin{aligned} \frac{\partial \Psi}{\partial c} &= \sigma_{ij} : \frac{\partial \left[ \varepsilon_{ij}^t - \frac{1}{3} \left( \Omega c + \lambda \int_0^t c dt \right) \delta_{ij} \right]}{\partial c} + \mu_0 + RT \ln \hat{c} + zF\varphi \\ &= \mu_0 + RT \ln \hat{c} - \sigma_{ij} : \left( \frac{1}{3} \Omega \delta_{ij} + \frac{1}{3} \frac{\partial \left( \lambda \int_0^t c dt \right)}{\partial c} \delta_{ij} \right) + zF\varphi \\ &= \mu_0 + RT \ln \hat{c} - \frac{1}{3} \sigma_{kk} \Omega - \frac{1}{3} \sigma_{kk} \frac{\partial \left( \lambda \int_0^t c dt \right)}{\partial c} + zF\varphi \end{aligned} \quad (\text{S6})$$

where the hydrostatic pressure  $\sigma_h = 1/3 \sigma_{kk}$ . Hence, the electrochemical potential  $\mu_{\sigma}$  is expressed as:

$$\mu_{\sigma} = \mu_0 + RT \ln \hat{c} - \Omega \sigma_h - \frac{\partial \left( \lambda \int_0^t c dt \right)}{\partial c} \sigma_h + zF\varphi \quad (\text{S7})$$

Here, we suppose that the change of the concentration within a short time can be expressed as  $\zeta \cdot t$ , where  $\zeta$  is the chemical reaction rate factor. According to Law of mass action, dimension of  $\lambda$  will change as electrochemical reactions change. In other words,  $\lambda$  is a reaction-dependent variable. Notably, dimension of  $\zeta$  will also change as  $\lambda$  changes. Thus, the electrochemical potential  $\mu_{\sigma}$  is given by:

$$\mu_{\sigma} = \mu_0 + RT \ln \hat{c} - \Omega \sigma_h - \left( \frac{\lambda \int_0^t c dt}{\zeta t} \right) \sigma_h + zF\varphi \quad (\text{S8})$$

Ions diffusion satisfies the law of mass conservation:

$$\frac{\partial c}{\partial t} = \nabla (Mc \nabla \mu) \quad (\text{S9})$$

where  $M$  is the ion mobility.

Substituting Equation (S8) into (S9) gives:

$$\frac{\partial c}{\partial t} = D \frac{\partial}{\partial x} \left\{ \frac{\partial c}{\partial x} - \frac{c}{RT} \frac{\partial \Omega \sigma_h}{\partial x} - \frac{c}{RT} \frac{\partial \left( \frac{\lambda \int_0^t c dt}{\xi t} \right) \sigma_h}{\partial x} + \frac{c}{RT} \frac{\partial z F \varphi}{\partial x} \right\} \quad (\text{S10})$$

where  $D=MRT$  is the ion diffusivity. Without the consideration of stress, chemical reaction, and electric field, Equation (S10) will reduce to the classic diffusion formula:

$$\frac{\partial c}{\partial t} = D \frac{\partial}{\partial x} \left( \frac{\partial c}{\partial x} \right) \quad (\text{S11})$$

Initial concentration of the guest ions in the actuator film is assumed to be zero:

$$c(x, 0) = 0 \quad (\text{S12})$$

Interface between substrate and actuator film acts as the dividing line between ion-existent region ( $\text{XS}_2$ ) and ion-inexistent region (metal foil), ion flux is considered to have no variation along the thickness direction at this interface. Therefore, the boundary condition at the interface is given by:

$$D \frac{\partial c(0, t)}{\partial x} = 0 \quad (\text{S13})$$

Since cyclic voltammetry measurement is carried out in this work, species concentration at the surface of the actuator film is therefore determined by the applied electrical potential. Theoretically, the charge transfer at SEI should be equilibrium. The electron transfer is considered to be rapid enough to satisfy the Nernst equilibrium.

Therefore, boundary condition at the surface of the actuator film is expressed as:

$$c(h_a, t) = c_0 \left\{ 1 - \exp \left[ \frac{(\varphi - \varphi_0)nF}{RT} \right] \right\} \quad (\text{S14})$$

where  $\varphi_0$  is the formal potential of system,  $c_0$  is the source concentration of guest ions in electrolyte. Since both oxidation and reduction reactions occur during electrochemical measurements,  $c_0$  could be converted into the concentration of oxidized or reduced species in solution.

### ***Curvature evolution***

In order to study the ions migration along the thickness direction ( $x$ -direction), the actuator film is considered as a large plate in  $y$  and  $z$ -directions. According to the classical Euler-Bernoulli beam theory, plane section remains plane after deformation, this hypothesis means that shear deformations equal zero. Shear stresses also equal zero during pure bending actuation. Moreover, stress along  $x$ -direction equals zero. As a first approximation,  $y$  and  $z$ -directions in large plate are assumed to have the same concentration distribution of guest ions. Thus, we postulate that the stresses along  $y$  and  $z$ -directions are equal, *i.e.*,  $\sigma_{zz} = \sigma_{yy}$ . Actuation force, which is another important factor for ECAs, mainly consists of the following parts:

$$\sigma_a = \sigma_{yy} = \sigma_{zz} = \sigma_i - \sigma_d - \sigma_r \quad (\text{S15})$$

The in-plane stress is a function of the distance from calculated point to neutral axis of the ECA  $x$  and curvature  $\kappa$ :

$$\sigma_i = Y_a (\varepsilon_0 + \kappa x) \quad (\text{S16})$$

where  $Y_a$  is the Young's modulus of the actuator film,  $\varepsilon_0$  is the strain at the interface between substrate and actuator film.

The second term of Equation (S15) represents the diffusion-induced stress:

$$\sigma_d = Y_a c \Omega \quad (\text{S17})$$

Both of the theoretical and experimental studies have demonstrated that chemical reaction will also cause a volume strain by affecting the formation of reaction compound. Thus, the third term is used to describe the chemical reaction-induced stress:

$$\sigma_r = Y_a \lambda \int_0^t c dt \quad (\text{S18})$$

Substituting Equation (S16)-(S18) into (S15) gives:

$$\sigma_a = Y_a (\varepsilon_0 + \kappa x) - \frac{Y_a}{3} \left( c \Omega + \lambda \int_0^t c dt \right) \quad (\text{S19})$$

Since substrate is assumed to be perfectly bonded to the actuator film, the stress in substrate is solely influenced by the in-plane strain:

$$\sigma_s = Y_s (\varepsilon_0 + \kappa x) \quad (\text{S20})$$

where  $Y_s$  is the Young's modulus of substrate.

There are no mechanical loads applied on the surfaces of substrate and actuator film, mechanical equilibrium conditions are therefore expressed as:

$$\int_{-h_s}^{h_a} \sigma_a dx = 0 \quad (\text{S21})$$

$$\int_{-h_s}^{h_a} \sigma_a x dx = 0 \quad (\text{S22})$$

where  $h_a$  and  $h_s$  represent the thicknesses of actuator film and substrate, respectively.

Respectively substituting Equation (S19) into (S21) and (S22) gives:

$$\varepsilon_0 \int_{-h_s}^{h_a} Y_a dx + \kappa \int_{-h_s}^{h_a} Y_a x dx = \frac{Y_a}{3} \int_0^{h_a} \left( c \Omega + \lambda \int_0^t c dt \right) dx \quad (\text{S23})$$

$$\varepsilon_0 \int_{-h_s}^{h_a} Y_a x dx + \kappa \int_{-h_s}^{h_a} Y_a x^2 dx = \frac{Y_a}{3} \int_0^{h_a} \left( c \Omega + \lambda \int_0^t c dt \right) \kappa dx \quad (\text{S24})$$

The curvature is obtained by:

$$\kappa = \frac{BG-AH}{B^2-AE} \quad (\text{S25})$$

where

$$\begin{aligned}
 A &= \int_{-h_s}^{h_a} Y_a dx & B &= \int_{-h_s}^{h_a} Y_a x dx & E &= \int_{-h_s}^{h_a} Y_a x^2 dx \\
 G &= \frac{Y_a}{3} \int_0^{h_a} \left( c\Omega + \lambda \int_0^t c dt \right) dx & & & & (S26a-e) \\
 H &= \frac{Y_a}{3} \int_0^{h_a} \left( c\Omega + \lambda \int_0^t c dt \right) x dx
 \end{aligned}$$

### **Performance parameters**

Gravimetric capacitance  $\bar{C}$  of the working electrode is calculated by:

$$\bar{C} = \frac{\int IdV}{2 \cdot v \cdot \Delta V \cdot m} \quad (S27)$$

where  $V$  and  $I$  are the applied voltage and current, respectively.  $v$  is the scan rate,  $\Delta V$  is the voltage range,  $m$  is the weight of the actuator film.

Energy density  $W$  is one of the most important parameters to evaluate the actuation performance:

$$W = \frac{1}{2} Y \varepsilon^2 \quad (S28)$$

where  $\varepsilon = \Delta\kappa \cdot x$  is the bending-induced strain,  $\Delta\kappa$  is the curvature change from initial state to calculated state (*i.e.*, actuated state at some time). Young's modulus of the bilayer ECA  $Y$  is given by:

$$Y = Y_s \cdot \frac{h_s}{h_s + h_a} + Y_a \cdot \frac{h_a}{h_s + h_a} \quad (S29)$$

Power density  $W_p$  is a measurement of power output per unit volume:

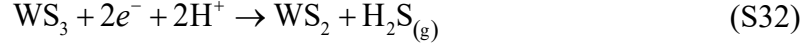
$$W_p = \frac{W}{t} \quad (S30)$$

where  $t$  is the time for one cycle. The gravimetric power density  $W_{p-g}$  can be obtained by dividing the density of the ECA  $\rho$ :

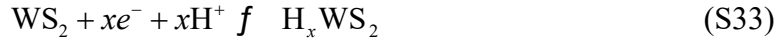
$$W_{p-g} = \frac{W}{\rho t} \quad (S31)$$

### ***Charge storage behavior***

The presence of WS<sub>3</sub> contributes to hydrogen adsorption:

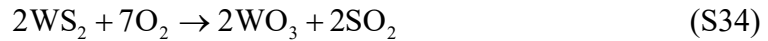


Then, both of the obtained WS<sub>2</sub> and the original WS<sub>2</sub> nano-onions will interact with the intercalated hydrogen ions:

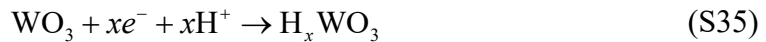


The remaining hydrogen ions then keep migrating into deeper region of the nanosheets and the same interaction is repeated until  $x$  of H <sub>$x$</sub> WS<sub>2</sub> reaches its maximum. Here,  $x$  is in the range of  $0.012 < x < 0.84$ . The value of  $x$ , which varies during redox reaction, reflects the bonded degree between hydrogen ions and WS<sub>2</sub>. Thus, different  $x$  values correspond to different atomic volumes of reaction compounds, and thereby result in varied expansion degrees of the actuator film.

After long-term interaction, WS<sub>2</sub> near the surface of nano-onions will convert to WO<sub>3</sub>:



The generation of WO<sub>3</sub> is beneficial for adsorbing hydrogen:



Quantity of the electrical charges  $Q$  changes as potential  $E$  in pseudocapacitive reaction, and thereby results in capacitance  $dQ/dE$ . The proportion of the region dominated by surface and near surface reaction to total region of host materials  $X$  is related to the potential  $E$ :

$$E \sim E^0 - \frac{RT}{nF} \ln\left(\frac{X}{1-X}\right) \quad (\text{S36})$$

where  $E^0$  is the standard potential of the redox couple,  $n$  is the number of transferred charges during reaction.

Pseudocapacitive reaction contains intercalation of ions and surface redox reaction.

They can be distinguished from each other by:

$$i(V, \nu) = a\nu^b \quad (\text{S37})$$

where  $a$  is a constant related to surface area and diffusion rate of charges in host materials.  $b$  is the slope of the line in Figure 3f.  $b$ -values correspond to various kinetics properties. For instance, surface and near surface reaction corresponds to 1.0, bulk diffusion corresponds to 0.5. When  $b$ -value changes from 0.5 to 1.0, the electrochemical reaction is dominated by both of them:

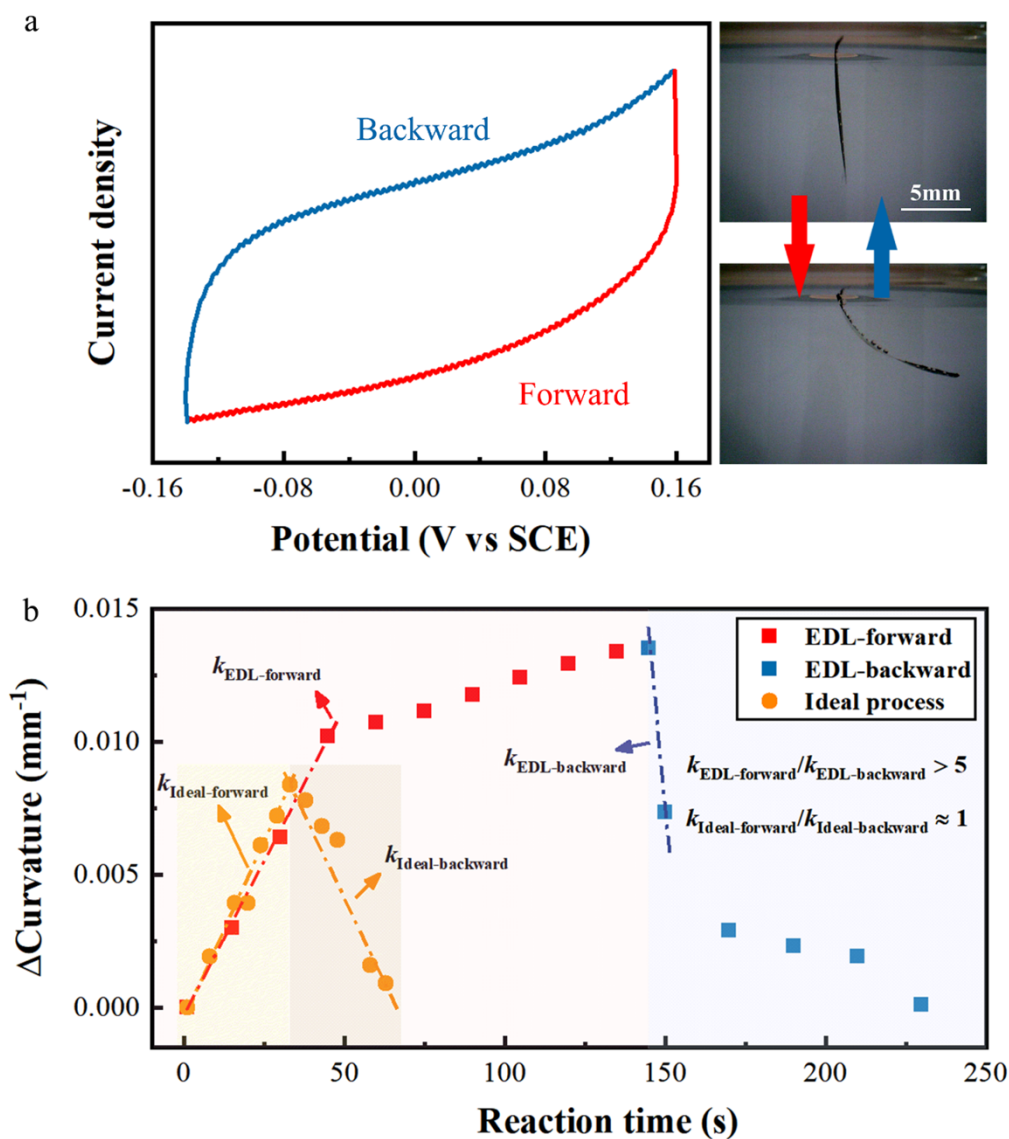
$$i(V, \nu) = k_1(V)\nu + k_2(V)\nu^{1/2} \quad (\text{S38})$$

where  $k_1$  and  $k_2$  are scan rate-independent constants. Equation (S38) can be further expressed as:

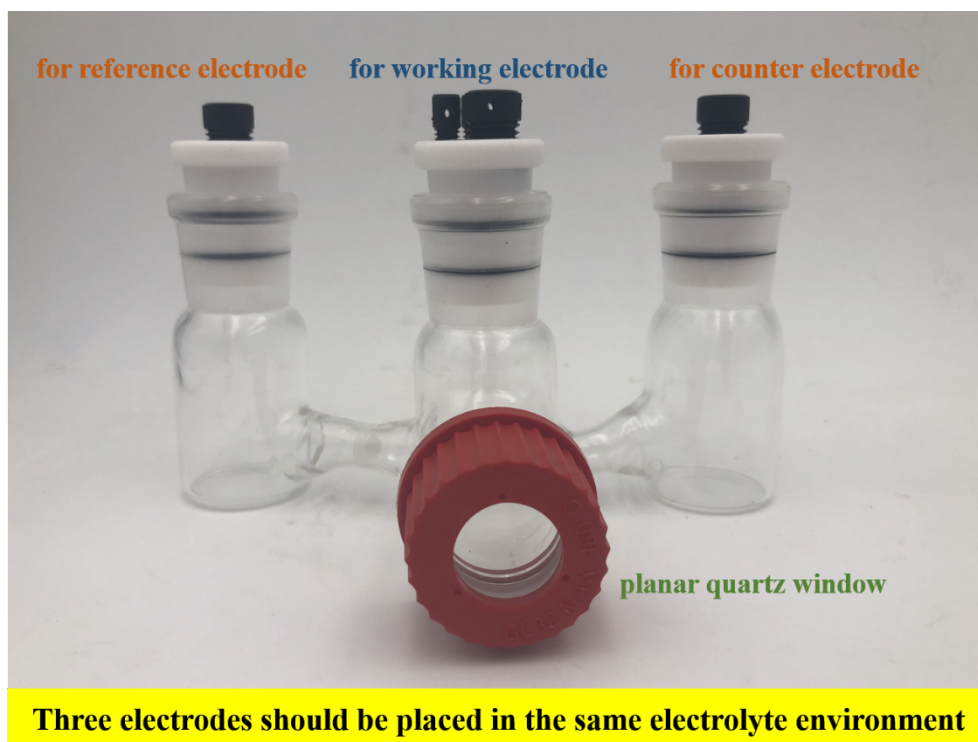
$$i(V, \nu)/\nu^{1/2} = k_1(V)\nu^{1/2} + k_2(V) \quad (\text{S39})$$

According to Equation (S39), the slope and the  $y$ -axis intercept of the straight line in the figure of  $i(V, \nu)/\nu^{1/2}$  vs  $\nu^{1/2}$  is  $k_1$  and  $k_2$ , respectively. The values of  $k_1$  and  $k_2$  can be fitted by substituting current  $i$  and scan rate  $\nu$  at each potential into Equation (S39). Then, the contributions of surface and near surface-dominated reaction and bulk diffusion can be distinguished from each other.

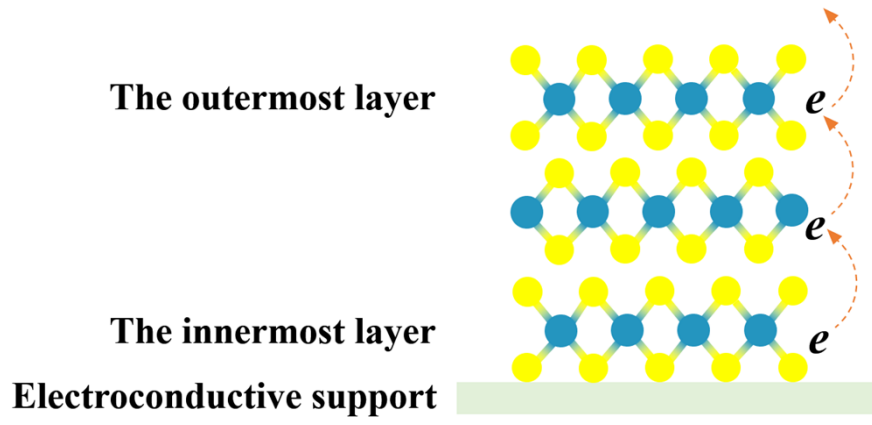




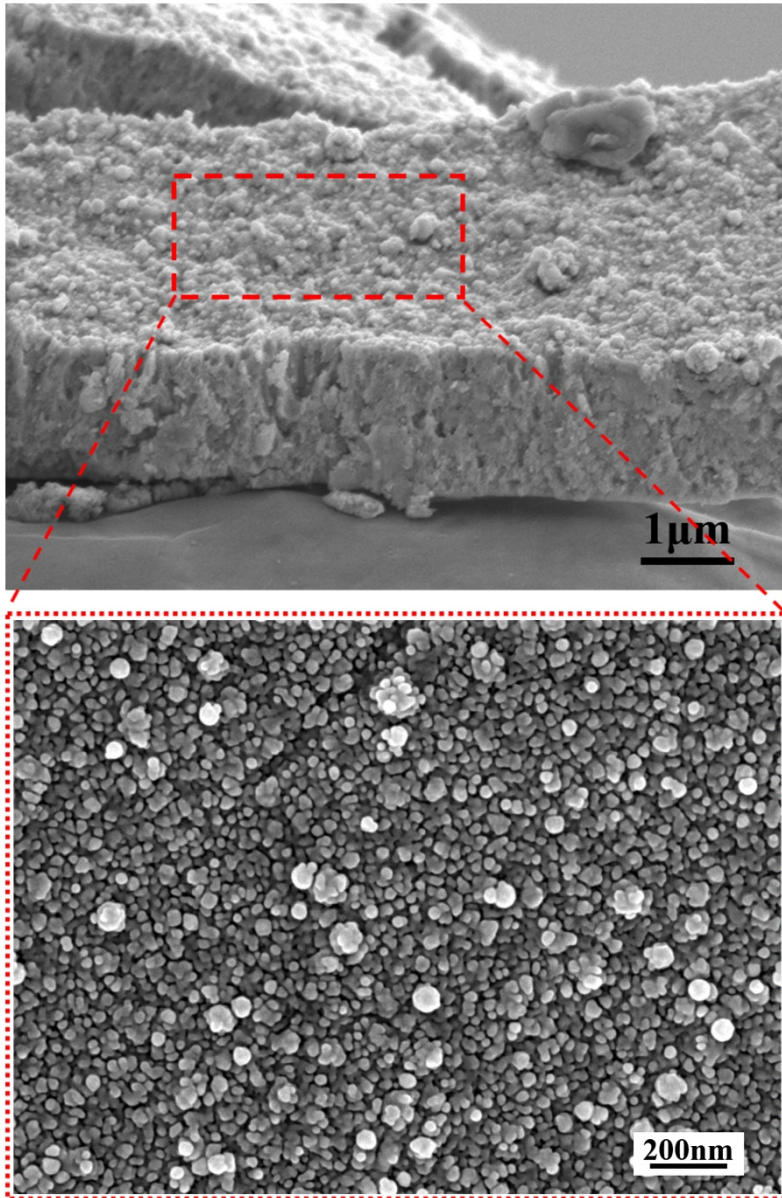
**Fig. S1.** (a) Symmetric EDL reaction process and the corresponding actuation process. The ‘symmetric’ means the centrosymmetric current-potential curve of cyclic voltammetry measurements. (b) Curvature evolutions during EDL reaction process and ideal process.  $k$  represents the rate of curvature change in forward and backward actuations.



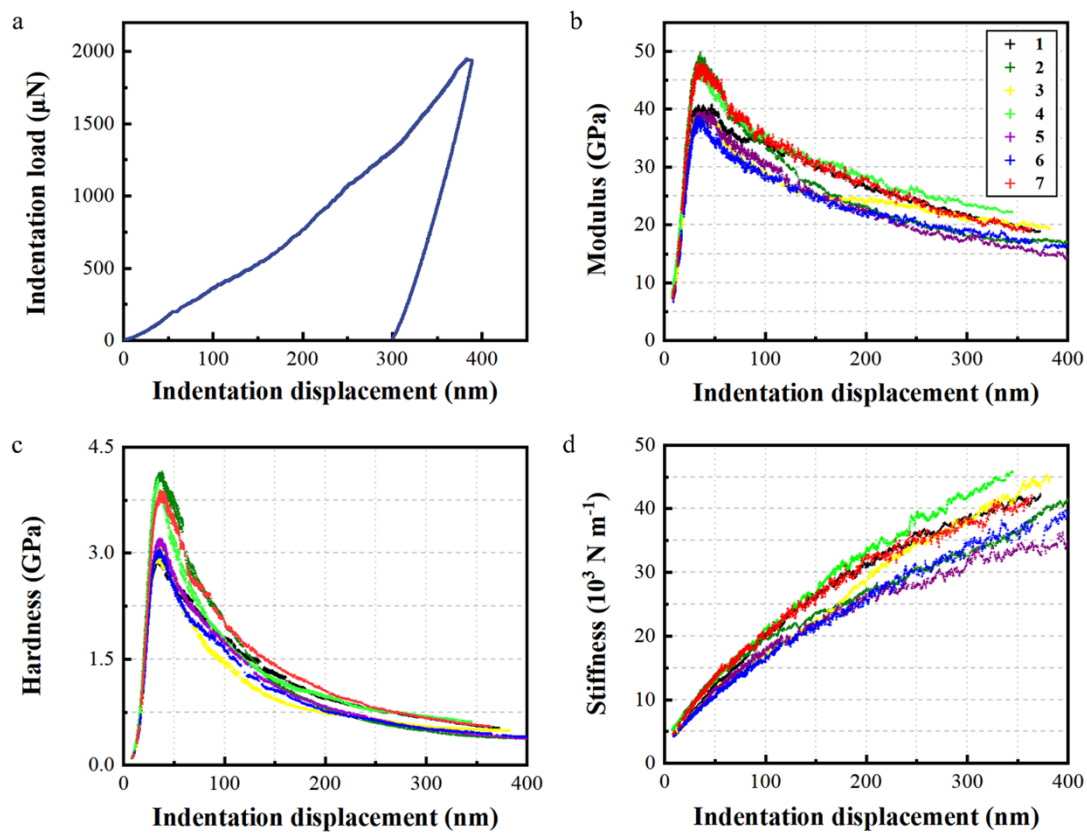
**Fig. S2.** Three electrode setup for electrochemical and in-situ actuation tests.



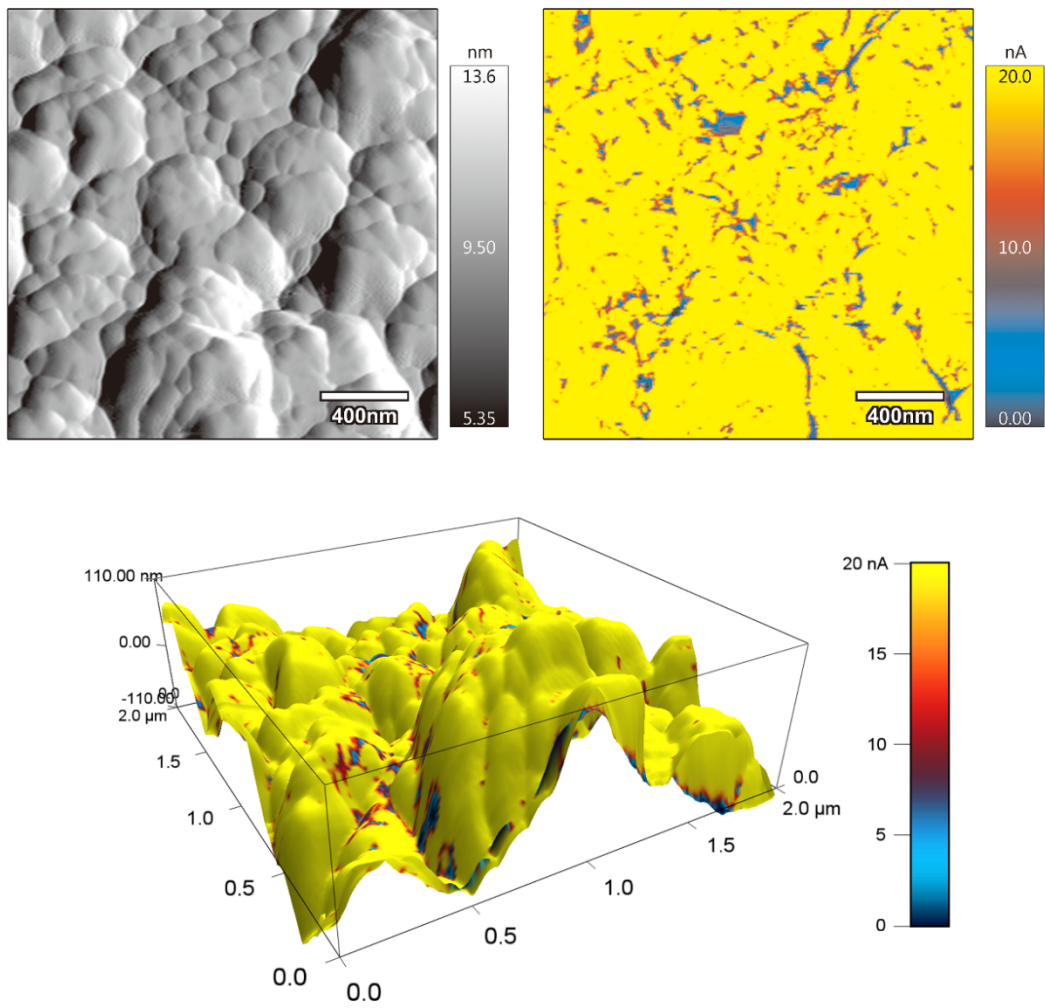
**Fig. S3.** Electron hopping across TMDs nanosheets in the perpendicular direction.



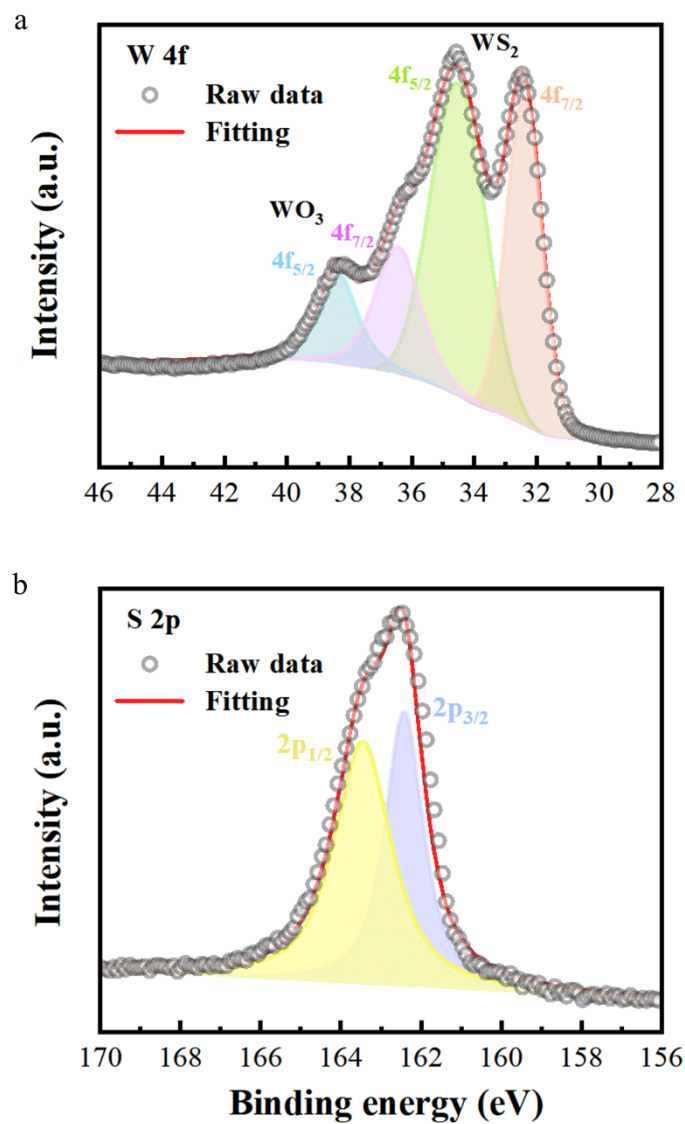
**Fig. S4.** SEM image of the actuator film.



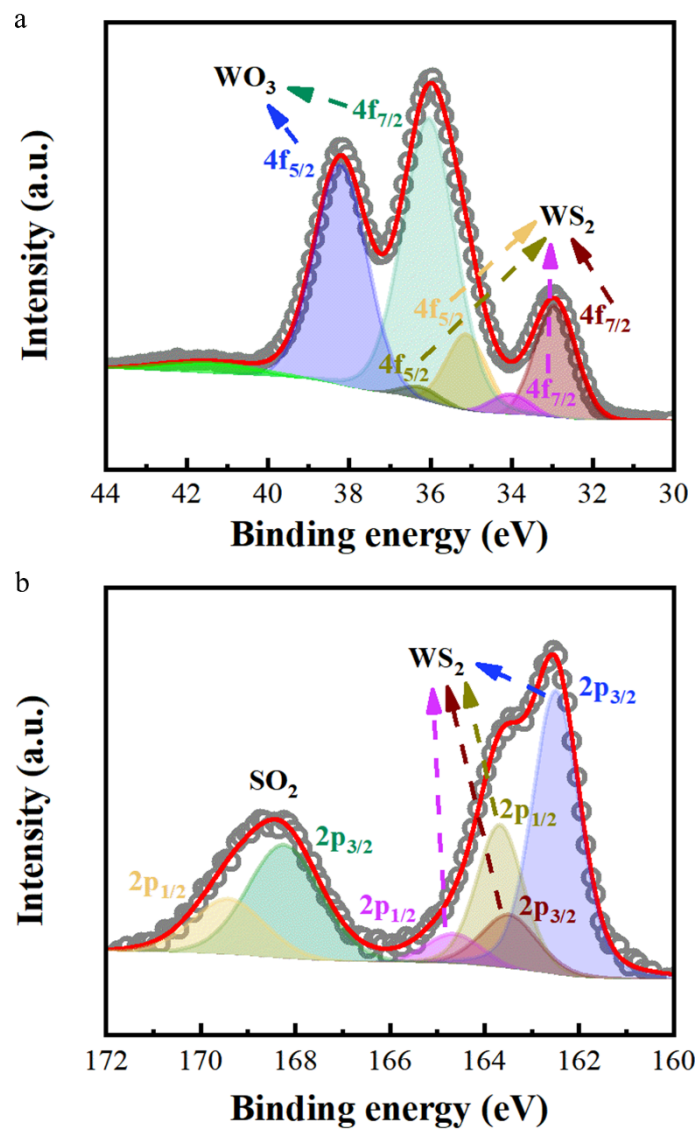
**Fig. S5.** Mechanical properties of 4  $\mu\text{m}$  actuator film. (a) Loading cycle of nanoindentation measurement. (b), (c), and (d) Modulus, hardness, and stiffness at varied positions of the actuator film, respectively.



**Fig. S6.** Topography and the corresponding cAFM images (at 40 mV) of the actuator film.

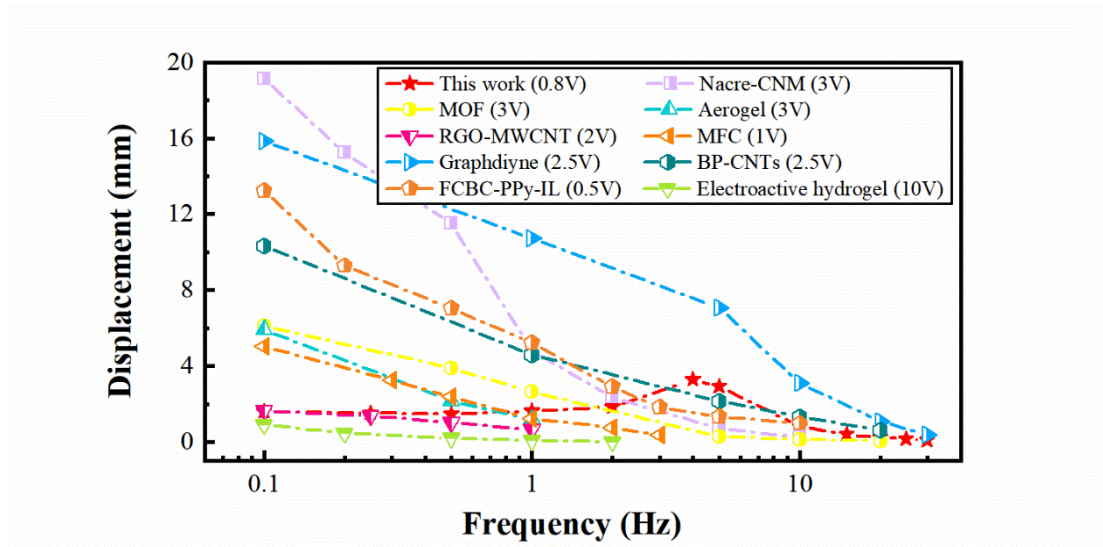


**Fig. S7.** XPS spectra for (a) W 4f and (b) S 2p regions of a thicker W-S shell, which comprises 5 to 6 layers of the nanosheets.



**Fig. S8.** XPS spectra for (a) W 4f and (b) S 2p regions after long-term cycles.





**Fig. S9.** The absolute values of the displacements corresponding to Fig. 4a of the main text. Note that these actuators have different lengths, widths and applied voltages. A larger absolute value of the displacement usually represents a more intuitive deformation. For the future applications of ECAs, intrinsic deformability, displacement level and the possibility of proportionally scaling the ECA samples in preparation should be simultaneously considered.