

## A self-powered electrochromic device driven by a nanogenerator†

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Electrochromic (EC) devices are capable of reversibly changing optical properties upon charge injection and extraction driven by an externally applied voltage. A nanogenerator (NG) is a device that converts mechanical energy into electricity. This paper demonstrates a self-powered EC device driven by an NG. An average visible optical modulation ( $\Delta T_{\text{vis}}$ ) as large as 15.3% was obtained, with electrochromic response time (ERT) and coloration efficiency (CE) of 10 seconds and  $58.7 \text{ cm}^2 \text{ C}^{-1}$ , respectively. Such a performance is comparable to an EC when powered by a hardwired DC power. This study indicates that the self-powered electrochromic system can be a candidate for monochrome displays or electronic billboards.

## Introduction

Due to advances in micro/nano-sized electronic devices, highly integrated and multifunctional electronic systems are becoming prevalent in people's daily life. With constantly improved performance and increasingly reduced size and weight, conventional power sources such as batteries may hinder independent and sustainable operation of these electronic systems.<sup>1-3</sup> A promising solution is to integrate a miniaturized energy-harvesting device into the system to realize self-powered operation.<sup>4,5</sup> Recently, aimed at harvesting mechanical energy in our living environment, NGs have been developed for converting small magnitude mechanical energy into electricity, including piezoelectric NG,<sup>6,7</sup> pyroelectric NG,<sup>8</sup> triboelectric NG,<sup>9,10</sup>

*etc.* Furthermore, trials on self-powered technology have been attempted with very promising results and potential applications.<sup>11,12</sup>

Electrochromic (EC) materials are capable of reversibly changing optical properties upon charge injection and extraction, which are driven by an externally applied voltage. They are currently attracting much interest because of low power consumption and high coloration efficiency<sup>13-16</sup> that make them suitable for a variety of applications such as smart windows, electronic billboards, as well as displays of portable and flexible devices including smart cards, price labels and electronic papers.<sup>17-23</sup> For example, tungsten trioxide ( $\text{WO}_3$ ), when injected with protons or other small monovalent cations such as  $\text{Li}^+$ , becomes dark blue with little power involved. Even lower power consumption is expected if  $\text{WO}_3$  nanoparticles are used for the electrochromic purpose.<sup>24</sup> Therefore, it is entirely possible to drive the electrochromic device by nanogenerators that scavenge energy from the environment such as airflow, vibration, sonic waves, human activity and so on.<sup>25</sup> In this paper, we developed two kinds of self-powered systems by integrating a  $\text{WO}_3$ -based electrochromic device with a nanogenerator for potential applications in monochrome self-powered displays in portable electronic devices as well as in electronic billboards.

## System design and characterization

Fig. 1a and b show schematic diagrams of self-powered EC systems. The power source unit has an NG and a full-wave bridge for rectification. The NG converts mechanical energy into electricity, while the full-wave bridge transforms alternating current from the NG to unidirectional current. In this work, two types of self-powered EC systems are designed. In the first approach, the electricity generated by the NG is rectified and stored in a capacitor and then released to drive the EC device (Fig. 1a). The charging process and discharge process are controlled by a regular switch (blue dashed rectangle in Fig. 1a). A reversible switch is for determining how the capacitor and the EC device are connected. In the second design, the NG was

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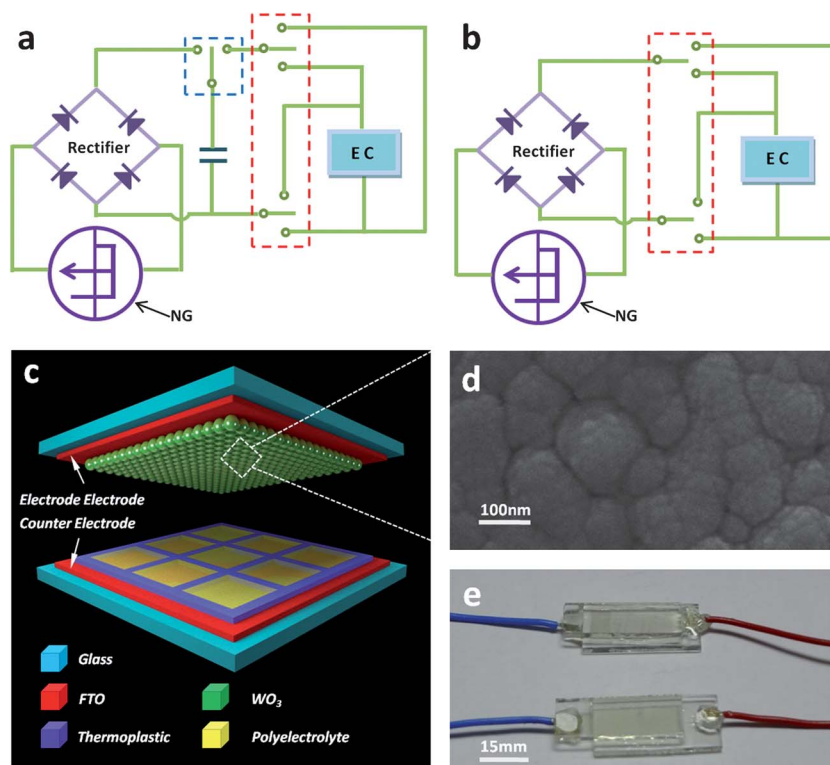
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## Broader context

This paper demonstrates a self-powered electrochromic device driven by a nanogenerator. An average visible optical modulation ( $\Delta T_{\text{vis}}$ ) as large as 15.3% was obtained, with electrochromic response time (ERT) and coloration efficiency (CE) of 10 seconds and  $58.7 \text{ cm}^2 \text{ C}^{-1}$ , respectively. Such a performance is comparable to an EC when powered by a hardwired DC power. This study indicates that the self-powered electrochromic system can be a candidate for monochrome displays or electronic billboards. This billboard-type display will not be supplied with any power from outside sources and will not contribute to carbon emissions.



**Fig. 1** Schematic diagram of the self-powered electrochromic device (EC) system and the structure of the  $\text{WO}_3$ -based EC device. (a) NG-charged power source; (b) real-time power supply; (c) the structure of the  $\text{WO}_3$ -based EC device; (d) SEM image of the  $\text{WO}_3$  film; (e) a picture of the EC device.

connected to the EC device through a full-wave rectifier without an energy storage unit as an *in situ* power supply (Fig. 2b). There is also a reversible switch for reversing the connection polarity between the NG and the EC unit.

The EC unit has a multi-layered structure, which is sketched in Fig. 1c. The outer layers are commercially purchased glass substrates covered with FTO thin films on one side as electrodes, which have a sheet resistance and transmittance of 35–45  $\Omega$  per sq. and 80%, respectively. Until otherwise noted, all transmittance data in this paper are on the basis of visible light. Sandwiched between the two electrodes are an array of cells that are filled with polyelectrolyte and a layer of  $\text{WO}_3$  film of about 250 nm that consists of densely packed nanoparticles (Fig. 1d). The fabrication process is discussed in more detail in the Experiments and methods section. The distance between the two electrodes is around 20  $\mu\text{m}$ . As demonstrated in Fig. 1e, the fully packaged EC device still has a transmittance of more than 70%.

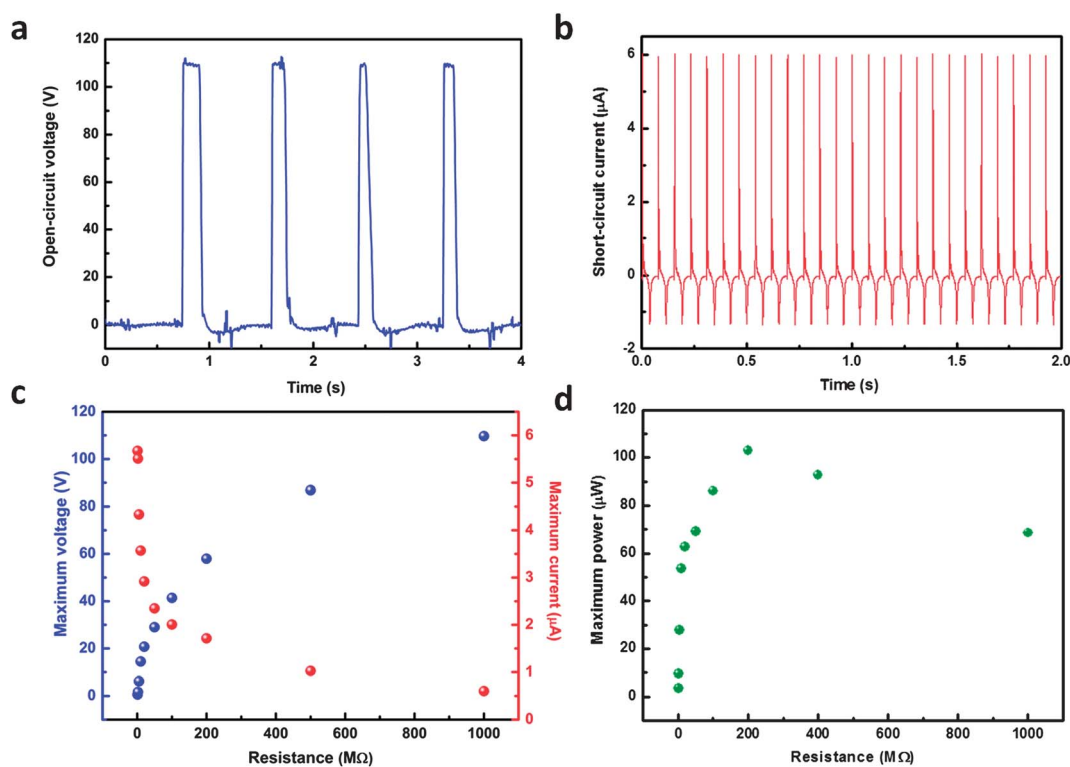
The NG has two different polymer layers between which a cavity is sustained by a spacer. Owing to the coupling of contact charging and electrostatic induction, electricity generation is achieved by a cyclic process of contact and separation between two polymer films. The fabrication process and working principle were presented in detail previously.<sup>10</sup> The performance of the NG is characterized by measuring open-circuit voltage ( $V_{\text{oc}}$ ) (Fig. 2a) and short-circuit current ( $I_{\text{sc}}$ ) (Fig. 2b). The instantaneous  $V_{\text{oc}}$  and  $I_{\text{sc}}$  reached up to 100 V and 6  $\mu\text{A}$ , respectively. When an external load is applied, the output voltage and current of the NG are dependent on the value of the load resistance, as demonstrated in Fig. 2c. Fig. 2d indicates that the maximum power of 9  $\mu\text{W}$  can be obtained at a load resistance of 2 M $\Omega$ .

We define a forward connection when the working electrode (WE) as shown in Fig. 1c is connected to the negative end of a power

source. If a power source with reverse polarity is applied, a reverse connection is established. The electrochromic response (ER) time during the coloring process and bleaching process is calculated on the basis of 80% change of transmittance. To investigate the performance of the self-powered EC systems that are demonstrated in Fig. 1, a mechanical vibration at a frequency of 6 Hz was applied to the NG.

## Results and discussion

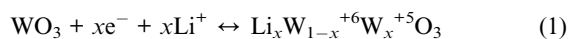
In the first type of the systems (Fig. 1a), the voltage across the capacitor reached 4 V after being charged for 14 seconds. Subsequently, the capacitor was forwardly connected to the EC device and discharged. In the discharging process, the voltage across the EC device and the current flowing through it were simultaneously monitored, with results presented in Fig. 3c (left section). Once the capacitor starts to discharge, the current surges to a maximum value and decreases sharply, which is accompanied by the drop of transmittance of an EC cell called the coloring process. The result is visualized in Fig. 3a with a clearly darkened area. In contrast, with reversed connection by putting the reversible switch (Fig. 1a) to another position, the voltage and current exhibit the same behavior (right section of Fig. 3c), the EC cell recovers to transparency, corresponding to a bleaching process (Fig. 3b). In the meantime, the transmittance spectrum of the EC cell was recorded, as shown in Fig. 3d. Compared with the as-fabricated cell, the transmittance of the colored cell considerably drops, with average visible optical modulation amplitude ( $\Delta T_{\text{vis}}$ ) calculated to be 15.3% (see ESI†). It is further noticed that a relatively stable difference of as much as 17% in transmittance is maintained for wavelength that ranges from 450 nm to 650 nm. The result is an indication that the EC system is sensitive



**Fig. 2** The performance characterization of the nanogenerator. (a) Open-circuit voltage; (b) the short-circuit current; (c) the dependence of the voltage and current on the external resistance value; (d) the dependence of the instantaneous power on the external resistance value.

and thus applicable to a broad range of light wavelength. After the colored cell is bleached, the transmittance fully recovers. The ER time for both the coloring and bleaching processes is even less than 10 seconds.

The reversible change in transmittance is caused by transfer of mobile ions,  $\text{Li}^+$  in this case, between the electrolyte and the  $\text{WO}_3$  film. Driven by an external voltage, the  $\text{Li}^+$  ions are injected into the  $\text{WO}_3$  film, corresponding to the coloring process. If a voltage of reverse polarity is subsequently applied, the  $\text{Li}^+$  ions can be extracted from the  $\text{WO}_3$  film; and the colored film is bleached. The reversible change can be expressed by the following reaction



where  $x$  is the insertion coefficient and  $0 < x < 1$ .

In the second design of the systems (Fig. 2b), the voltage across the EC device, the current through it and its transmittance at a wavelength of 650 nm were recorded simultaneously. Figs. 4a–c represent a set of measured results for forward connection. It needs to be pointed out that every data point on the voltage and the current curves represents the instantaneously maximum peak value as shown in Fig. 2a and b, respectively. As the NG continues to provide electric power, the voltage across the EC device gradually rises because of the increasing resistance of charge transfer as more and more  $\text{Li}^+$  ions fill into the  $\text{WO}_3$  film. By the same reasoning, the current through the EC device drops. Such a trend is in accordance with the result shown in Fig. 2c. Similar to the first type of design, repeatable coloring and bleaching processes were obtained, with  $\Delta T_{\text{vis}}$  in this case calculated to be 5.9%. The visualized results are presented in Fig. 4d with a clearly observable difference.

Besides, the amount of charge transferred per unit colored area can be calculated by the equation below,<sup>26</sup>

$$Q = \frac{\int_{t_1}^{t_2} i dt}{S} \quad (2)$$

where  $t_1$  is the starting time when external voltage is applied,  $t_2$  is the time when the EC cell is fully colored/bleached,  $i$  is the current through the EC device and  $S$  is the area of the EC device.

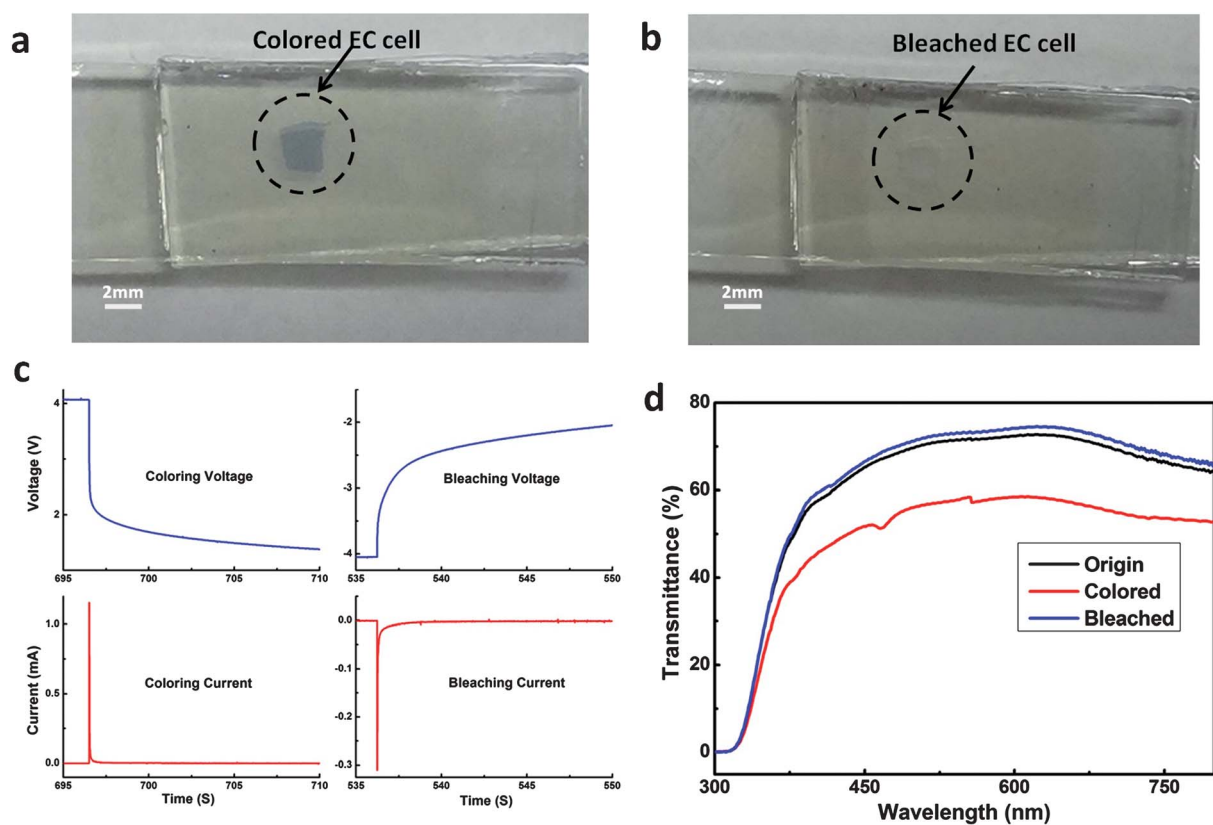
For the first design, within the ER time, the  $Q$  for coloring and bleaching processes are  $1.4 \times 10^{-3} \text{ C cm}^{-2}$  and  $1.3 \times 10^{-3} \text{ C cm}^{-2}$ , respectively. The  $Q$  value for the second design increases linearly with time (Fig. 4d), reaching  $2.0 \times 10^{-4} \text{ C cm}^{-2}$  (coloring) and  $2.4 \times 10^{-4} \text{ C cm}^{-2}$  (bleaching) at ER time. Therefore, charge transfer of almost equal quantity occurs during the reversible electrochromic modulation, indicating complete reversibility. The coloration efficiency is expressed as,

$$\text{CE} = \log(T_b/T_c)/Q$$

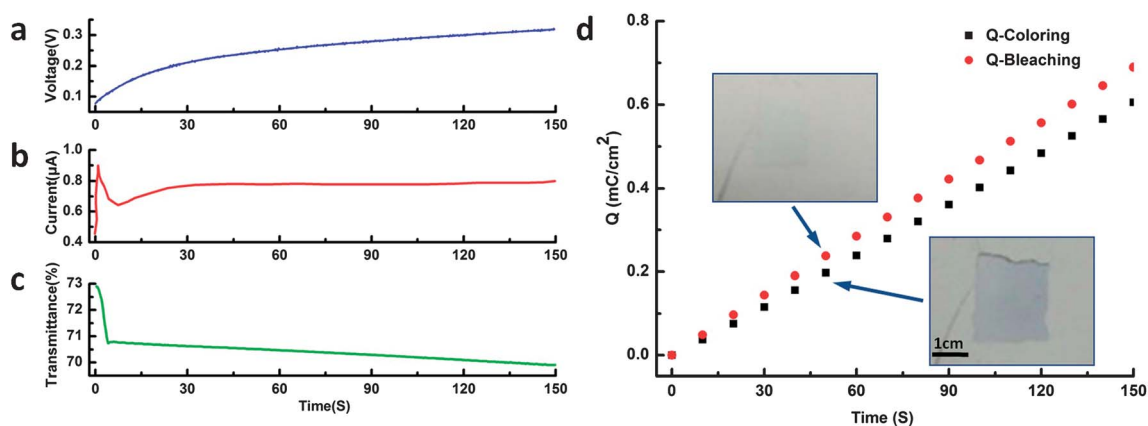
where  $T_c$  and  $T_b$  are the transmittance of the EC-cell at 650 nm in the colored and bleached states.

Such a value is calculated to be  $58.7 \text{ cm}^2 \text{ C}^{-1}$  and  $20.3 \text{ cm}^2 \text{ C}^{-1}$  for our first and second designs, respectively, which are comparable to some of the recent reports on  $\text{WO}_3$ -film-based electrochromic devices.<sup>26–28</sup>

For the purpose of further comparison, a square wave signal (1.5 V, 2 Hz) generated by a hardwired power source was applied to replace the NG. The measurement results are presented in the ESI<sup>†</sup>, which reveal that our self-powered systems are comparable



**Fig. 3** The testing results of a self-powered EC device driven by NG-charged power. (a) The optical image of the colored EC; (b) the optical image of the bleached EC; (c) the  $I_t$  and  $V_t$  of coloring (left pair) and bleaching processes (right pair); (d) the transmittance spectra of the EC in as-fabricated, colored and bleached states.



**Fig. 4** The testing results of an EC device with real-time power supply. (a)  $V_t$  of the process of coloring; (b)  $I_t$  of the process of coloring; (c) the transmittance of the process of coloring; (d) the charge per unit area ( $Q$ ) participating in the coloring/bleaching process and pictures of colored and bleached states.

to the hardwire-power-driven EC device in terms of transmittance modulation, ER time and coloration efficiency (see ESI†).

## Conclusion

An integrated module is presented in this paper in the form of a combination of a nanoparticle- $\text{WO}_3$  film electrochromic device and a nanogenerator, for demonstrating the potential of monochrome self-powered displays. This self-powered EC-device showed desirable ER

times and high CE values. Furthermore, the EC device can be made on a flexible substrate and integrated with our flexible nanogenerator to be a kind of wearable device.

## Experiments and methods

### Preparation of $\text{WO}_3$ nanoparticle film (electrochromic layer)

The  $\text{WO}_3$  nanoparticle film was prepared by using RF sputtering under the condition of  $\text{O}_2 : \text{Ar} = 16 : 24$ , the sputtering power was



140 W and the sputtering time was 30 minutes. The sputtering target was tungsten oxide and the purity 99.99%. The thickness of the film as measured by a profilometer was about 250 nm.

### Fabrication of electrochromic device

The counter electrode was prepared by placing a 25  $\mu\text{m}$  thick hot melt sealing foil (DHS-SN1760) frame with a 2 mm  $\times$  2 mm cell which is cut in advance and heated at 100  $^{\circ}\text{C}$  for 5 min. Then, drop a 10  $\mu\text{l}$  polyelectrolyte in the cell and put the electrochromic counter ( $\text{WO}_3$ -FTO film) on the top, hold the two counters together with the cramp and heat at 100  $^{\circ}\text{C}$  for 3 min to form a sandwich-type electrochromic device. Finally, wire electrodes were adhered by using Leitsilber 200 conductive silver paint for the following test.

### Preparation of polyelectrolyte

The polyelectrolyte was prepared by completely dissolving  $\text{LiClO}_4$  in CAN (acetonitrile) and subsequently mixing with PMMA, stirred and volatilized for 12 h. The proportion of  $\text{LiClO}_4$ , CAN and PMMA is 3 : 50 : 10.

### Assembly of measuring system

The measuring system is made of a spectrophotometer, a computer, a low-noise voltage preamplifier and a current preamplifier. The electrochromic device (EC) is fixed on the sample holder between the light source and the detector, the working electrode and counter electrode are connected with the nanogenerator (NG) power source unit. The optical testing unit is sealed as a camera obscura. The  $I_t$ ,  $V_t$  and transmittance spectra are measured at the same time.

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