

Fast-Switching Photovoltachromic Cells with Tunable Transmittance

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Smart windows, which control the light entering buildings, aircraft, and cars, have received increasing attention because of their proficiency in saving energy. Electrochromic¹ and photochromic² materials with reversible transmittance in response to an applied voltage and illumination, respectively, are the most common materials for smart windows.³ An alternative, the photoelectrochromic cell (PECC), was demonstrated in 1996.⁴ PECC has a configuration similar to that of dye-sensitized solar cells (DSSCs).⁵ Both employ a dye-sensitized TiO₂ nanoparticle (NP) film as the photoanode, but the Pt counter-electrode of DSSCs is replaced by WO₃ electrochromic film in PECC. Under illumination, photoelectrons generated at the anode move to the WO₃ electrode *via* an external circuit, which drives Li⁺ ions in the electrolyte to intercalate into WO₃, forming Li_xWO₃ for coloration. The colored cell is bleached in the dark at short circuit, but the bleaching rate is rather slow. PECC has also been constructed using a Pt counter-electrode and adding WO₃ to the photoanode, where Pt (a catalyst) can accelerate the bleaching independently of the coloration.^{6,7} For both PECCs, coloration is attained by the photon-electron conversion, with no need for external power sources. However, their associated photovoltaic characteristics have not been demonstrated. In the present study, we report a novel photovoltachromic cell (PVCC), composed of a patterned WO₃/Pt electrochromic electrode and dye-sensitized TiO₂ NP photoanode, which has both photoelectrochromic and photovoltaic characteristics. Under light illumination, the PVCC can be colored at short circuit with tunable transmittance and it can be bleached exceed-

ABSTRACT In this study, we demonstrate a photovoltachromic cell (PVCC) which is a solar cell and able to take solar energy to stimulate chromic behavior with the characteristic of tunable transmittance. The cell is composed of a patterned WO₃/Pt electrochromic electrode and a dye-sensitized TiO₂ nanoparticle photoanode. Compared to reported photoelectrochromic cells (PECC) with nonpatterned WO₃ electrochromic electrodes, PVCC achieves a much faster bleaching time of only 60 s by blocking the light at short circuit. When PVCC is bleached under illumination at open circuit, an exceedingly short bleaching time of 4 s is achieved. Furthermore, PVCC has photovoltaic characteristics comparable to those of dye-sensitized solar cells (with Pt as the counter-electrode). In contrast to conventional photochromic devices, the transmittance of PVCC under a constant illumination can be adjusted by the resistance of a load in series with the cell. These characteristics are a result of the patterned WO₃/Pt electrode, which provides effective charge transfer pathways to facilitate the charging/discharging of Li ions and electrons *via* the photovoltaic potential and the Pt-electrolyte catalytic route, respectively.

KEYWORDS: photovoltaic device · photoelectrochromic cell · photovoltachromic cell · charge transfer · fast response · tunable transmittance

ingly fast by simply opening the circuit. This unique performance results from the crucial charge transfer pathways provided by the patterned WO₃/Pt electrochromic electrode. The proposed PVCC thus establishes a scheme for constructing a self-powering, fast-response, transmittance-tunable smart window, and for constructing a self-powering, contrast-adjustable display when the PVCC cells are fabricated pixel-by-pixel.

RESULTS AND DISCUSSION

The proposed PVCC with a patterned WO₃/Pt film as the electrochromic electrode and a PECC with the same configuration as that demonstrated in 1996 (schematics shown in Figure 1A) were fabricated using identical WO₃ (320 nm thick), photoelectrodes and electrolytes. Both cells can be colored under illumination at short circuit. Transmittance spectra of the as-prepared and colored (after AM 1.5 illumination (100 mW/cm²) for 1 min) PECCs, measured at open circuit, are shown in

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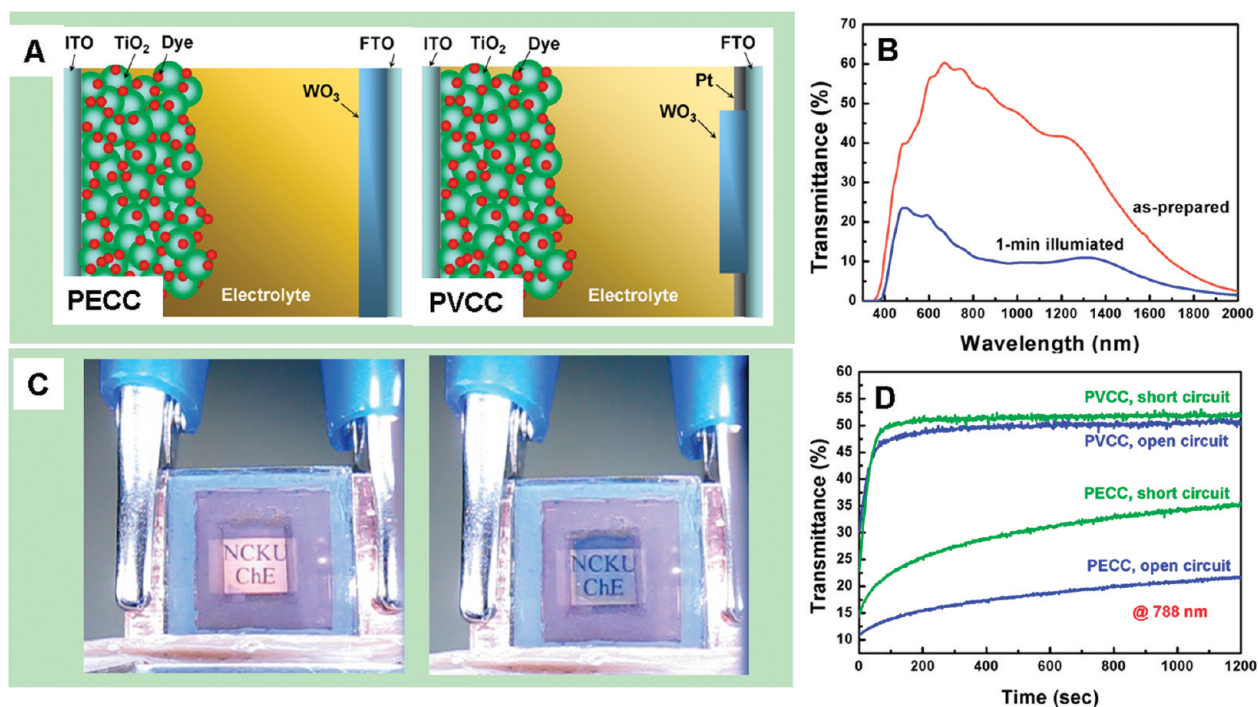


Figure 1. (A) Schematics of PECC and PVCC. (B) Transmittance spectra of PECC in the as-prepared and the colored states, measured at open circuit. (C) Photographs of PVCC in the as-prepared (left) and colored (right) states. The colored photograph was taken at short circuit under illumination. The illumination makes the background letters rather clear even though the PVCC is colored. (D) Evolutions of cell bleaching at a wavelength of 788 nm for open- and short-circuited PECC and PVCC in the dark.

Figure 1B. The transmittance spectrum of illuminated PVCC at open circuit is almost identical to that of the as-prepared one, making it seem as though there is no colored state for PVCC. Figure 1C reveals that an apparent blue color can be observed with naked eyes on PVCC under illumination at short circuit. The orange and blue colors observed on the as-prepared and colored PVCCs are attributed to the dyes adsorbed on the photoelectrode and to Li_xWO_3 formed in the electro-

chromic electrode, respectively. The bleaching of PVCC at open circuit is so fast that the colored transmittance spectrum cannot be exactly recorded. Therefore, the time evolution of cell bleaching was further monitored using a monowavelength beam.

The cells were first colored under a white-light LED illumination of $\sim 4 \text{ mW/cm}^2$ intensity for 1 min. After the LED radiation was turned off, evolutions of cell bleaching at open circuit in the dark were monitored at 788 and 632 nm wavelengths, as shown in Figure 1D and Figure S1 (Supporting Information), respectively. The figures show that PVCC indeed has a significantly faster response of cell bleaching and that the transmittance of PVCC in the colored state (at $t = 0$) is higher than that of PECC. In addition, Figure 1D illustrates that, compared to bleaching at open circuit, the bleaching rate is substantially faster at short circuit for PECC but the difference is not as significant for PVCC. For a cell fabricated using a WO_3/FTO -patterned electrochromic electrode, as shown in Figure 2A (I), the open-circuit and short-circuit bleaching rates are comparable (Figure 2B) but they are inferior to those of the WO_3/Pt -patterned cell (PVCC). Moreover, the fast bleaching response is not obtained in a modified WO_3/Pt -patterned cell in which only WO_3 is exposed to the electrolyte, as shown in Figures 2A (II) and 2C. These observations indicate that the bleaching rate is optimal when Pt contacts both WO_3 and the electrolyte simultaneously. The charge transfer between Pt and electrolyte thus plays a crucial role in the bleaching process of PVCC.

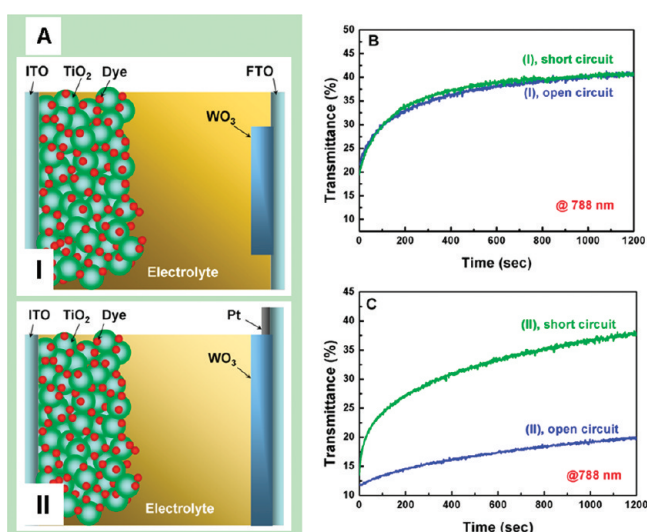


Figure 2. (A) Schematics of cells with various electrochromic electrodes: (I) WO_3/FTO -patterned cell and (II) WO_3/Pt -patterned cell in which only WO_3 is in contact with the electrolyte. (B) Evolutions of bleaching at a wavelength of 788 nm for open- and short-circuited cell-I in the dark. (C) Evolutions of bleaching at a wavelength of 788 nm for open- and short-circuited cell-II in the dark.

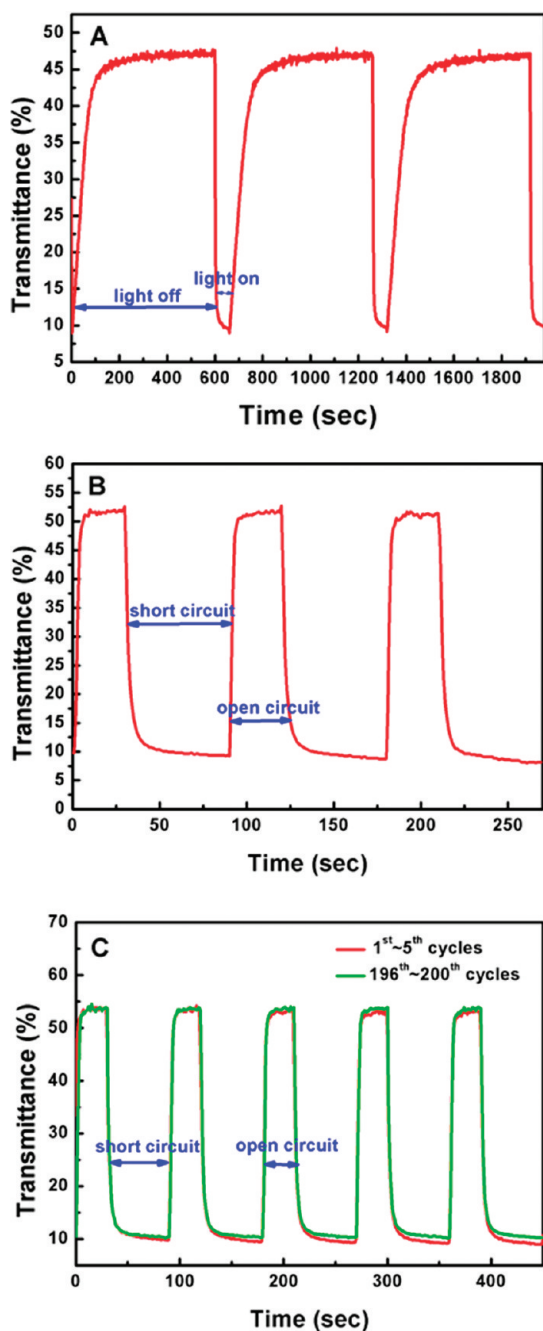


Figure 3. Change in transmittance of PVCC measured at 788 nm: (A) exposed to chopped white light at short circuit; (B) subjected to open/short cycles under illumination; (C) stability of PVCC performance under illumination after 200 open/short cycles. (Light source: white-light LED with an intensity of 4 mW/cm²).

The thickness of WO₃ film on the electrochromic electrode was further increased to 880 nm, which darkened the colored state of PVCC to a transmittance of around 10% at a wavelength of 788 nm. The transmittance of coloration–bleaching cycles for the short-circuited PVCC on exposure to chopped white light (4 mW/cm²) was monitored at a wavelength of 788 nm, as shown in Figure 3A. The coloration time (T_c) and bleaching time (T_b) are defined as the times where the transmittances change by two-thirds of the difference be-

TABLE 1. Photovoltaic Properties of DSSC, PECC, and PVCC under AM 1.5 Illumination at 100 mW/cm^{2a}

cell	J_{sc} (mA/cm ²)	V_{oc} (V)	F.F.	η (%)
DSSC	2.38	0.58	0.34	0.46
PECC	0.67	0.06	0.21	0.01
PVCC	2.23	0.57	0.40	0.50

^a J_{sc} , V_{oc} , F.F., η are the short-circuit current density, open-circuit voltage, fill factor, and efficiency of the cells, respectively.

tween the steady-state transmittances in bleached and colored states.⁸ Accordingly, when exposed to chopped white light, T_c (with light on) and T_b (with light off) of the PVCC at short circuit are about 4 and 60 s, respectively.

PVCC can also be bleached under illumination by opening the circuit. The change in transmittance during short-open cycles at a wavelength of 788 nm of the illuminated PVCC is shown in Figure 3B. When the cell terminals under illumination were opened, T_b of the PVCC was reduced to be only around 4 s. This is significantly faster bleaching compared to that *via* the blocking of light (Figure 3A). In contrast, the enhancement of the bleaching time was not observed for the PECC at open circuit and under illumination (Figure S2, Supporting Information). The stability of PVCC under illumination was further tested by subjecting it to 200 open/short cycles. Figure 3C shows that the coloration–bleaching response curves are almost identical for 200 open/short cycles, demonstrating very good stability of the PVCC.

Figure 4A illustrates the photovoltaic characteristics of the DSSC (Pt as the counter-electrode), PECC, and PVCC with the same photoelectrode and electrolyte measured under AM 1.5 illumination at 100 mW/cm². Their photovoltaic properties are listed in Table 1. The efficiency of DSSCs is affected by the reduction rate of I_3^- back to I^- at the counter-electrode.⁹ The inferior photovoltaic performance of the PECC is ascribed to the slow I_3^-/I^- reduction rate on the WO₃ surface, leading to insufficient [I^-] in the electrolyte for dye regeneration. When a WO₃/Pt-patterned film is employed as the electrochromic electrode, PVCC attains photovoltaic characteristics comparable to those of DSSC, as shown in Table 1, indicating that this chromic cell is able to serve as an efficient solar cell. Owing to its photovoltaic characteristics, the operating current and voltage of PVCC can be controlled by connecting an external load (resistance = R)¹⁰ and the optical transmittance subsequently varies. To prove this idea, we measured the change in optical transmittance of the illuminated PVCC (with a white-light LED with an intensity of ~ 4 mW/cm²) in series with a variable resistor (2.5–800 Ω); the results are shown in Figure 4B. In contrast to conventional photochromic devices, the transmittance of the PVCC under a constant illumination can be varied by adjusting the resistance of a load in series with the

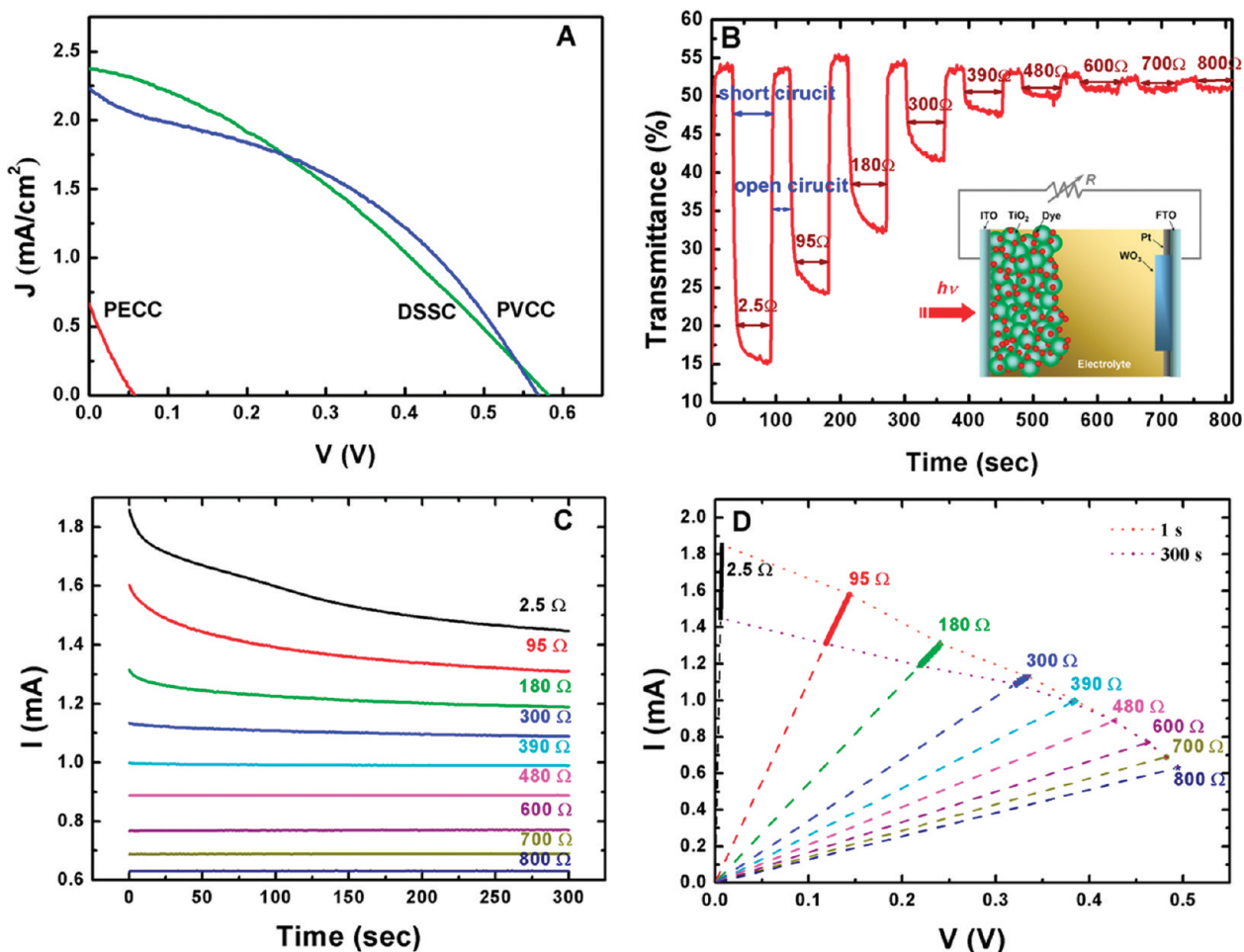


Figure 4. (A) J - V curves of DSSC, PECC, and PVCC under AM 1.5 illumination at 100 mW/cm²; (B) transient optical transmittance at 788 nm of PVCC in series with a variable resistor under illumination (with white-light LED with an intensity of 4 mW/cm²); (C) time evolutions of the current in the circuit of the illuminated PVCC (with a white-light LED with an intensity of \sim 4 mW/cm²) in series with a variable resistor; (D) time dependence of the I - V traces of the illuminated PVCC (with white-light LED with an intensity of 4 mW/cm²) in series with a resistor.

cell. To the best of our knowledge, this is the first demonstration of a PECC with evident photovoltaic characteristics and continuously variable transmittance.

Time evolutions of the current in the circuit of the illuminated PVCC (with a white-light LED with an intensity of \sim 4 mW/cm²) in series with a resistor were measured as shown in Figure 4C. The figure shows that the current decays to a constant when the series resistance $R < 480 \Omega$. On the other hand, the current remains constant (since $t = 0$) when the series resistance $R \geq 480 \Omega$. It should be noted that the decay of the current with time is consistent with the gradual decrease of the transmittance of the colored PVCC with time when the series resistance $R < 480 \Omega$, as shown in Figure 4B. Figure 4D shows the time dependence of the I - V traces of the illuminated PVCC in series with a resistor. When the series resistance is lower than 480 Ω , the evolution of the I - V traces follows the load lines (where $V = IR$) of the series resistors. The (I , V) data obtained with various series resistances at the same instant of time (for example, $t = 1$ s or $t = 300$ s) resemble the photovoltaic

I - V curves of PVCC. The results prove that PVCC has photovoltaic characteristics during and after the coloring process. Therefore, this cell is not only self-powered for its electrochromic function, but is also able to supply power to an external load.

According to Figure 4C,D, when the PVCC drives a load of lower resistance, a larger current and a less positive voltage appear across the cell. During coloring, the current is the sum of electron streams flowing through the WO₃ and Pt portions of the electrochromic electrode. The electron flow through WO₃ is accompanied by the charging of Li ions. Once the charging of Li ions into WO₃ is saturated, the electrical current becomes constant, which is attributed to the electrons flow through Pt only. When PVCC is in series with a resistor of high resistance, a substantially positive potential is built up at the electrochromic electrode. This does not favor the charging of Li ions into WO₃, so the saturated concentration of Li ions in the WO₃/Pt-patterned electrochromic electrode is reduced. Subsequently, the PVCC is less colored (higher transmittance). The mea-

sured current is mainly ascribed to the electrons flowing through the Pt portion of the electrochromic electrode.

Charge transfer in PVCC was investigated using electrochemical impedance spectroscopy (EIS). For comparison, EIS measurements on PECC and DSSC were also performed. The characteristics of the EIS spectra were examined using the method demonstrated by Adachi *et al.*¹¹ As shown in Figure 5, EIS spectra of PVCC and DSSC obtained at open-circuited potential (V_{oc}) exhibit the same three-arc characteristics with peak frequencies at around 520, 5.2, and 0.58 Hz, which are assigned to the impedance of electron transfer at the Pt counter-electrode, the impedance of electron transfer at the photoelectrode, and the finite Warburg impedance of I_3^- in the electrolyte, respectively.¹¹ In the case of PECC, the cell was still blue-colored after a 20-min EIS measurement was performed at V_{oc} due its large T_b (Figure S2, Supporting Information), indicating that the bleaching proceeded slowly during the measurement. Two arcs with peak frequencies at 1.7 kHz and 3.2 Hz, respectively, followed by a straight line in the low frequency range were observed in the Nyquist plot. They correspond to the impedance of the charge transfer at the WO_3 electrode, the impedance of the electron transfer at the photoelectrode, and the Warburg impedance of Li^+ in WO_3 film with the onset of finite length effects, respectively.^{12,13} The EIS analysis shows that PVCC has DSSC characteristics at the bleached state, that is, at open circuit under illumination, which confirms that electron transfer occurs only at the Pt portion of the electrochromic electrode in PVCC at V_{oc} . Therefore, when the WO_3 film is saturated with Li ions or when the charging of Li ions is impeded by a positive potential, WO_3 becomes inactive and PVCC behaves simply like a DSSC with the Pt portion serving as the active counter-electrode. The WO_3 /Pt-patterned electrode thus constructs pathways for charge transfer and subsequently determines the tunable-transmittance behavior of PVCC.

The fast bleaching process of PVCC, as compared to that of PECC, was further examined by measuring the time evolutions of potentials across the PVCC and PECC at open circuit, in the dark and under illumination. Figure 6A shows that the cells were initially colored under illumination at short circuit. After the colored cell was open-circuited and the light was simultaneously turned off, a negative potential was observed at the WO_3 /Pt-patterned electrochromic electrode of PVCC. The potential became more positive during the bleaching process, which can be ascribed to the contact between Pt and Li_xWO_3 film. The contact provides a path for the extraction of electrons from the colored Li_xWO_3 film; Pt releases electrons to the electrolyte *via* the catalytic reaction of $I_3^- + 2e^- \rightarrow 3I^-$. This charge transfer pathway enhances the extraction of electrons and leads to the discharge of Li ions from the colored Li_xWO_3 film dur-

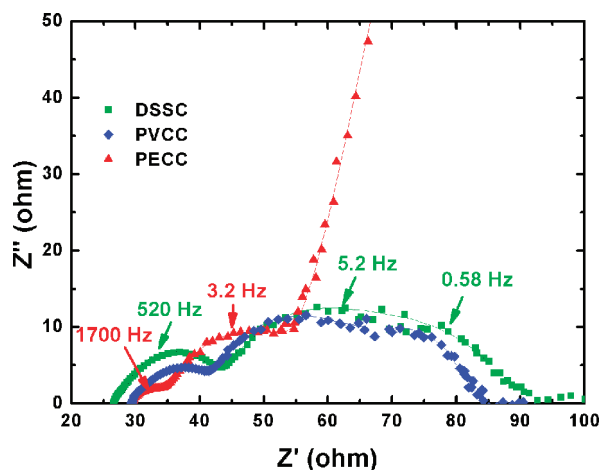


Figure 5. Nyquist plots of impedance data for DSSC, PECC, and PVCC measured at V_{oc} .

ing bleaching. However, since the potential of the electrochromic electrode in the PVCC stays negative during bleaching at open circuit in the dark, the discharge of positive Li ions is basically driven by the concentration gradient (*i.e.*, by diffusion). The bleaching rate is mainly determined by the diffusion rate of the positive Li ions in the electrochromic electrode. In the case of

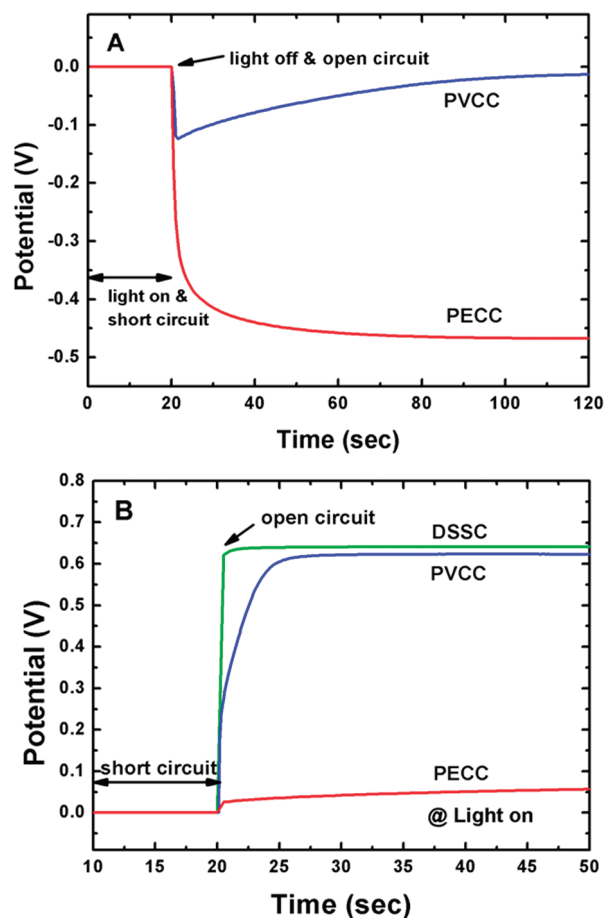


Figure 6. (A) Evolutions of the potentials across PECC and PVCC during bleaching at open circuit in the dark. (B) Evolutions of the potentials across DSSC, PECC, and PVCC during bleaching at open circuit under illumination.

PECC, the potential built up at the electrochromic electrode is more negative than that of PVCC and stays at a constant negative value, as shown in Figure 6A, which indicates that the discharge of Li ions proceeds very slowly; this is consistent with the large T_b in PECC via the bleaching process (Figure 1D). It should be noted that during the coloring of PVCC, electrons are also extracted from the partially colored Li_xWO_3 via Pt to the electrolyte. This results in a higher transmittance for the colored PVCC than that of the colored PECC (initial data points in Figure 1D and Figure S1). Nevertheless, the issue of high transmittance in the colored state can be resolved by increasing the thickness of WO_3 film in PVCC, as shown in Figure 3.

When PVCC is bleaching at open circuit under illumination (with white-light LED with an intensity of 4 mW/cm²), a positive potential is built up at the electrochromic electrode immediately after the cell circuit is opened, as shown in Figure 6B, as a result of the photovoltaic characteristic of PVCC. In contrast to the cell bleaching in the dark (where the Li ions are discharged by diffusion), the discharge of the positive Li ions from the Li_xWO_3 is drastically increased by the positive potential built at the electrochromic electrode under illumination. At the same time, electrons in the colored Li_xWO_3 electrode are released through the aforementioned Li_xWO_3 -Pt-electrolyte path. As a result, the potential approaches the V_{oc} of PVCC within 5 s, which matches well with the T_b of the PVCC under illumination (Figure 3B). The positive potential combined with the catalytic Pt at the electrochromic electrode increases the effec-

tive charge transfer to the electrolyte, which is not available in PECC, leading to an exceptionally fast bleaching rate of PVCC under illumination.

CONCLUSION

By employing a patterned WO_3/Pt electrochromic electrode and a dye-sensitized TiO_2 NP photoanode, we demonstrated a self-powered PVCC which exhibits distinct electrochromic characteristics of a fast switching rate and tunable transmittance under illumination. The patterned WO_3/Pt electrode brings Pt into contact with WO_3 and allows both Pt and WO_3 to transfer charges to the electrolyte individually. The charge transfer between Pt and the electrolyte gives PVCC significant photovoltaic characteristics. The fast open-circuit bleaching under illumination is achieved by the positive potential on the WO_3/Pt electrochromic electrode and the WO_3 -Pt-electrolyte channel, which facilitates the discharge of Li ions and electrons, respectively, from the colored WO_3 (*i.e.*, Li_xWO_3) to the electrolyte. The transmittance of PVCC can be tuned by modulating the number of Li ions and electrons into WO_3 , which is achieved by controlling the operating current and voltage on the WO_3/Pt terminal by driving an external load of variable resistance. This method can also be applied to build a self-powering and contrast-adjustable display when the PVCC cells are fabricated pixel-by-pixel. As a result, the proposed fast-response, energy-efficient, and transmittance-tunable PVCC has great potential for smart window and display applications.

METHODS

To prepare WO_3 films, tungsten powders were dissolved into a mixture of hydrogen peroxide and deionized water to form reflux for 12 h. The mixture was then vacuum-dried at 60 °C to obtain white particles. The white particles were dissolved in ethanol, and then poly(ethylene glycol) 2000 was added. WO_3 films were prepared by spin-coating the solution on FTO substrates and annealing them at 300 °C for 3 h. High resolution transmission electron microscopy (HRTEM) micrographs reveal a nanocrystalline WO_3 structure with a crystal size smaller than 5 nm embedded in an amorphous matrix (Figure S3, Supporting Information). To prepare the WO_3/Pt -patterned electrochromic electrode, Pt film was deposited using sputtering to encircle the WO_3 region. TiO_2 NP films were prepared by spin-coating P25 paste, which was formed by sonicating deionized water with P25, acetylacetone, and triton X-100, on ITO substrates, which were then calcined at 450 °C for 30 min. The thickness of the TiO_2 NP film was 3 μm . Dye adsorption was carried out by immersing the NP electrode in ethanolic solution of N719 dye ($\text{RuL}_2(\text{NCS})_2 \cdot 2\text{TBA}$; L = 2,2'-bipyridyl-4,4'-dicarboxylic acid and TBA = tetrabutylammonium) at 50 °C for 8 h. The photoelectrodes and electrochromic electrodes were sandwiched together with 60 μm -thick hot-melt Surlyn spacers. A liquid electrolyte solution composed of 0.5 M LiI and 5 mM I₂ in propylene carbonate⁶ was introduced between the two electrodes by capillary action. The cell area was 1.2 cm × 1.2 cm. The EIS measurements were carried out under an illumination of AM1.5 100 mW/cm² by applying a 10 mV ac signal over the frequency range of 10⁻²–10⁵ Hz on the top of V_{oc} of the corresponding cell using a potentiostat with a frequency response analyzer.

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Supporting Information Available: Evolutions of cell bleaching for open-circuited PECC and PVCC in the dark as well as for open-circuited PECC under illumination are provided. An HRTEM image of the WO_3 film is also presented. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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