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A Redox-Flow Electrochromic Window

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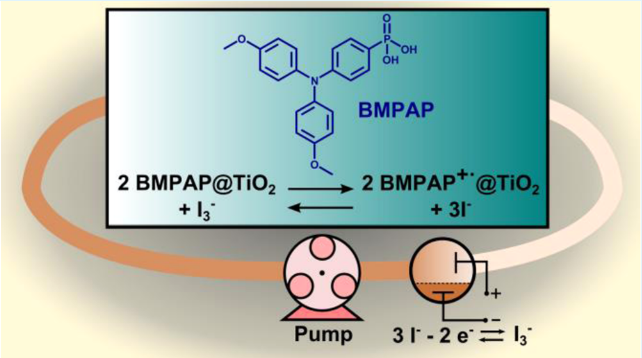
Supporting Information



ABSTRACT: A low-cost electrochromic (EC) window based on a redox-flow system that does not require expensive transparent conductive oxide (TCO) substrates is introduced and demonstrated for the first time. An aqueous I_3^-/I^- redox electrolyte is used in place of a TCO to oxidize/reduce a molecular layer of an EC triphenylamine derivative that is anchored to a mesoporous TiO_2 scaffold on the inner faces of a double-paned window. The redox electrolyte is electrochemically oxidized/reduced in an external two-compartment cell and circulated through the window cavity using an inexpensive peristaltic pump, resulting in coloration or decoloration of the window due to reaction of the redox solution with the triphenylamine derivative. The absorption characteristics, coloration/decoloration times, and cycling stability of the prototype EC window are evaluated, and prospects for further development are discussed.

KEYWORDS: *electrochromism, smart windows, redox-flow, triphenylamine, titanium dioxide, ioidide/triiodide*

■ INTRODUCTION

Electrochromic (EC) windows, also known as "smart windows" or "smart glass", can be darkened or lightened by application of an electrical bias, without the need for any mechanical input.[1] Common to all EC devices is one or more electroactive chemical species that change color when oxidized or reduced in an electron-transfer reaction. Several such materials have been evaluated for use in EC windows or displays, including inorganic materials such as WO_3,[2,3] NiO,[3] Prussian blue,[4] etc., and a wide range of organic materials not limited to viologens,[5,6] triarylamines,[7] polyanilines, and polythiophenes.[8−10] Presently, the most widespread commercial application of EC glass is in dimmable car rear-view mirrors, which employ a mixed bipyridilium-thiazine EC system.[11] Other potential uses for EC windows, which have not yet gained as much commercial traction, include controlling the amount of light and/or heat entering or leaving indoor spaces, increasing privacy, and modifying the aesthetics of rooms or buildings. Such commercial applications are presently hindered by long-term stability issues and high manufacturing costs,[12] the latter of which are heavily impacted by the use of relatively costly transparent conductive oxide (TCO) substrates, such as fluorine-doped tin oxide (FTO; commercially available for ~\$300/m^2 at the time of writing), in many of the most promising EC window designs.

To overcome the costs associated with TCO use, we developed a new class of TCO-free EC window that borrows concepts from the recently reported redox-flow lithium-ion battery.[13,14] The EC window, termed a redox-flow electrochromic window (RFEW), is essentially a transparent flow cell consisting of two sheets of inexpensive soda-lime glass separated by a gasket and coated with thin films of a solid EC material. A schematic diagram of the RFEW is shown in Figure 1. A redox mediator in solution is electrochemically oxidized or reduced in an external two-compartment cell and then pumped into the window cavity where a redox reaction occurs between the mediator and the EC material attached to the glass, leading to the desired coloration or decoloration of the window. Using this approach the TCO has effectively been replaced by redox-targeting technology,[15,16] which should yield significant cost reductions. Note that in replacing the TCO, additional costs associated with the external two-compartment cell and pump are introduced. However, these costs are expected to be minimal for large area windows (pump and external cell costs will not scale linearly with window area), and we believe that this new concept deserves attention.

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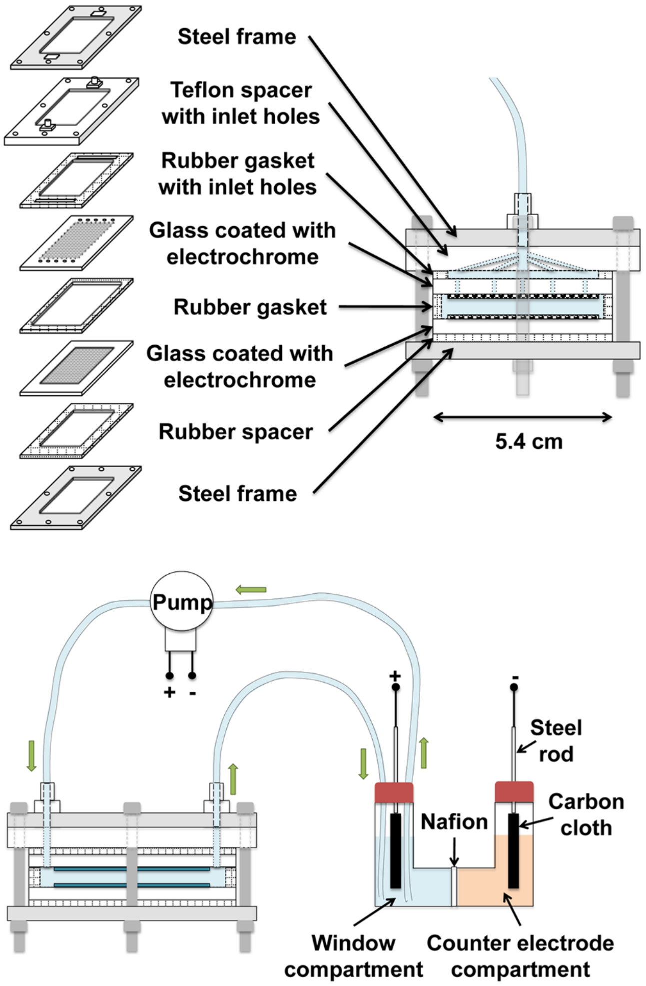

Figure 1. Schematic diagram of the redox-flow electrochromic window. A redox electrolyte solution is circulated between the window and an external two compartment cell using a peristaltic pump. Electrochromic molecules attached to the window interior are remotely switched between colorless and colored by oxidizing or reducing redox species in the electrolyte solution. Charge balance is maintained by oxidizing/reducing redox species in a counter electrode compartment that is connected to the main window compartment though a Nafion ion-selective membrane.

One might argue that the redox-targeting step in the RFEW, that is, the chemical reaction between the mediator and the solid film of EC material, is unnecessary. In principle, the electrochrome could simply be dissolved in in the electrolyte solution, oxidized or reduced in the external cell, and pumped into the window. Even more simply, a colorless solution in the cavity could be physically replaced with a colored solution by pumping and vice versa. However, these very simplistic approaches require that the electrochrome (or dye) employed has adequate solubility and extinction coefficient. On the contrary, by utilizing solid films, solubility is no longer an issue, and, since a significantly higher volume density of electrochrome can be obtained, the requirement for high extinction coefficient is also relaxed. Another advantage of the RFEW is that the counter electrode, and the associated electrolyte solution needed for charge balance, is entirely removed from the visible window area, further relaxing material requirements (i.e., these materials need not be colorless or transparent as they do in other EC window designs).

In the present article, we demonstrate one possible implementation of a, RFEW utilizing a triphenylamine derivative anchored to a mesoporous TiO_2 support as the electrochrome, and an aqueous I_3^-/I^- redox couple for redox-targeting. These components were chosen due to their limited reactivity with oxygen and water (at an appropriate solution pH), which enables operation of the RFEW under ambient conditions. The constituent parts of the system are first characterized by cyclic voltammetry and UV−vis−NIR spectroscopy, before being assembled into a prototype RFEW for further testing. The transmittance spectra, coloration/decoloration times, and stability are then evaluated and discussed.

■ EXPERIMENTAL METHODS

Device Fabrication. The window unit was constructed from two pieces of 8 cm × 5.4 cm × 3 mm soda-lime glass, separated by a 2 mm thick Viton brand rubber gasket. Five 1 mm diameter holes were drilled into each end of one of the pieces of glass to allow fluid to enter and leave the cavity between the pieces of glass. Prior to window assembly, an ∼6 μm thick layer of mesoporous TiO_2 (Dyesol, 18-NRT) covering a 6.5 cm × 4 cm area was deposited onto one face of each piece of glass by screen printing, followed by annealing according a previously reported temperature ramping procedure.[20] After annealing, the TiO_2 films were coated with a layer of (3-(4-(bis(4-methoxyphenyl)amino)phenoxy)propyl)phosphonate (BMPAP) by soaking them overnight in an ∼0.15 mM aqueous solution of the sodium salt of BMPAP. One side of the window was connected to the outlet of a peristaltic pump via Teflon fittings and tubing, and the other side was similarly connected to one side of a two-compartment cell (cf. Figure 1). The two-compartment cell was constructed of glass and employed an ∼1 cm^2 Nafion separator. Each compartment was capable of holding ∼4 mL of electrolyte solution. Electrodes made from ∼2 cm × ∼1 cm pieces of carbon cloth were inserted into each compartment, with both sides of the cloth exposed to the electrolyte solution (total exposed area ≈ 4 cm^2). One compartment was connected to the inlet of the peristaltic pump and to the outlet of the window unit via Teflon tubing. This compartment, termed the window compartment throughout this article, was filled with a pH 3.4 (HCl−glycine buffer) aqueous solution that was 1 mM in KI and 1 M in KCl. The total volume of solution used in each experiment was ∼13 mL. The peristaltic pump was continuously driven with 12 V provided by an adjustable power supply unless otherwise stated. This voltage produced a flow rate through the RFEW of ∼0.7 $cm^3\ s^{-1}$. The other compartment, termed the counter electrode compartment, was filled with a pH 3.4 aqueous solution that was 0.2 M in KI and was saturated with I_2 (<0.1 M). The solution in the counter electrode compartment was vigorously stirred with a magnetic stir bar during all experiments.

Electrochemical Measurements. Cyclic voltammetry experiments were performed using a conventional three-electrode setup with an Autolab potentiostat (Ecochemie). All experiments utilized a Ag/AgCl reference electrode (3.5 M KCl), a Pt wire counter electrode, and either a glassy carbon disc working electrode or a fluorine-doped tin oxide (FTO) working electrode that was coated with a 6 μm mesoporous TiO_2 film bearing an adsorbed molecular layer of BMPAP, which was prepared as described above.

Spectroscopic Measurements. UV−vis−NIR spectroscopy measurements were performed using a Shimadzu Solidspec-3700 spectrophotometer. The spectral and transient transmittance of the RFEW was recorded using a 300 W xenon arc lamp (Newport) coupled to a grating monochromator equipped with order sorting filters (Cornerstone 260, Newport) as light source and a silicon photodiode (Newport) connected to an autoranging current amplifier (Optical Power Meter, Newport) as detector.

■ RESULTS AND DISCUSSION

Chemical Constituents of the Prototype Redox-Flow Electrochromic Window. A triphenylamine derivative

(BMPAP, Figure 2)[16] adsorbed on mesoporous TiO_2 was used as the EC component of the RFEW. The oxidation potential of BMPAP is shifted negatively relative to unsubstituted triphenylamine by the addition of electron-donating alkoxy groups in the para position relative to the N atom on all three phenyl rings. On the basis of previous literature reports, such a modification is expected to shift the oxidation potential negatively by ∼0.40 V and should result in a very stable radical cation when oxidized in aqueous solution.[17] The $E_{p/2}$ potential for a related molecule, tris(4-methoxyphenyl)amine), is ∼0.72 V versus SHE in aqueous solution.

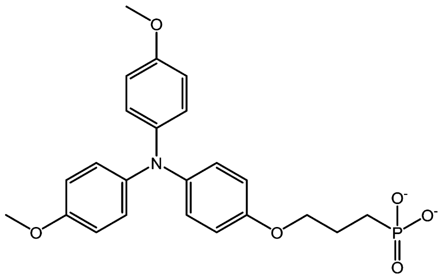

Figure 2. Molecular structure of (3-(4-(bis(4-methoxyphenyl)amino)-phenoxy)propyl)-phosphonate (BMPAP).

The I_3^-/I^- redox couple was identified as a suitable redox shuttle for remotely oxidizing and reducing BMPAP due to its similar half-wave potential in acidic aqueous solution.[18] Figure 3 shows a cyclic voltammogram recorded using a BMPAP-modified mesoporous TiO_2/FTO working electrode in pH 3.4 (HCl−glycine buffer), 1 M KCl aqueous solution. Aside from a very small shoulder at ∼0.55 V (presumably due to an impurity), the voltammetric response is quasi-reversible with an $E_{p/2}$ potential of 0.76 V versus SHE, very close to the reported value of 0.72 V for the similar compound tris(4-methoxyphenyl)amine). For comparison, a voltammogram of 5 mM KI (1 M KCl supporting electrolyte, pH 3.4 HCl−glycine buffer) on a glassy carbon electrode is also shown. The two pairs of peaks are believed to correspond to the I^-/I_2 (or I^-/I_3^-) and I_3^-/I_2 redox reactions.[19] Evidently, the $E_{p/2}$ potential for the first pair of quasi-reversible peaks (0.69 V) is close to that obtained for BMPAP. Assuming the $E_{p/2}$ potentials are close to the formal potentials, it should be possible to control the $[\text{BMPAP}^{+\cdot}]/[\text{BMPAP}]$ ratio in the TiO_2 film by immersing it in an I_3^-/I^- redox electrolyte solution and tuning the redox potential by varying the relative concentrations of I^- and I_3^-, provided also that the kinetics of the redox reactions between the two couples are sufficiently fast.

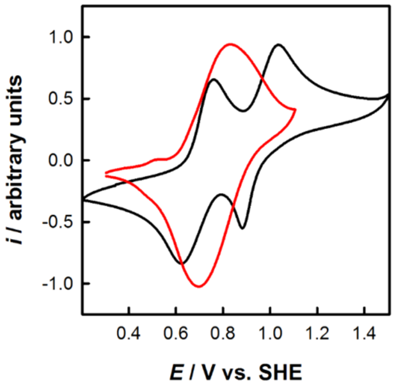

Figure 3. Cyclic voltammetry of RFEW components. The red curve shows a cyclic voltammogram recorded using an FTO/mesoporous TiO_2/BMPAP working electrode in a pH 3.4 (HCl−glycine buffer) aqueous 1 M KCl solution. The black curve shows a cyclic voltammogram recorded using a glassy carbon working electrode in a pH 3.4 aqueous solution that was 1 mM in KI and 1 M in KCl.

Electrochemical oxidation of the BMPAP film by application of 1 V for ∼1 min resulted in the appearance of a broad absorbance band in the visible to NIR range, causing the electrode to take on a bright blue appearance (Figure 4a). This coloration could be removed by application of 0.40 V for several minutes. The reactivity of BMPAP with I_3^- (or I_2) was tested by attempting chemical oxidation with an aqueous I_3^-/I_2 solution. A BMPAP-coated TiO_2 film was immersed and shaken for 1 min in an aqueous 0.1 M KI solution that was saturated with I_2. The film was then rinsed with distilled water to remove excess I_3^-/I_2. Oxidation of BMPAP was confirmed by the appearance of a similar broad absorption band centered at ∼730 nm (Figure 4b). In this case the electrode takes on a bright green coloration, presumably due to the additional presence of I_3^- counterions (which are in excess compared to I^- ions in the oxidizing solution). The coloration was found to be stable provided that the films were kept immersed in water. If exposed to air the color gradually faded but could be fully restored by further exposure to I_3^-/I_2 solution. We hypothesize that this is due to loss of I_2 to the atmosphere, leaving behind I^-, which subsequently reduces $\text{BMPAP}^{+\cdot}$ back to BMPAP. The reaction between $\text{BMPAP}^{+\cdot}$ and I^- was confirmed by exposing the freshly oxidized films to an aqueous 0.1 M KI solution, upon which the vis−NIR absorbance band and film coloration disappeared (Figure 4b). It was possible to cycle between colored and colorless states multiple times without any obvious loss of color.

Characterization of the Prototype Redox-Flow Electrochromic Window. As mentioned previously, the prototype RFEW tested in this work consisted of two BMPAP-coated TiO_2 films and an aqueous electrolyte solution containing 1 mM KI and 1 M KCl that was buffered at pH 3.4 by a HCl−glycine buffer. The pH was chosen to avoid water oxidation when applying an oxidizing bias to the electrode in the window side of the two-compartment cell, while at the same time minimizing oxidation of I^- by dissolved oxygen, which would cause unwanted spontaneous coloration of the window. The counter electrode compartment contained a pH 3.4 aqueous solution that was 0.2 M in KI and was saturated with I_2 (<0.1 M). The redox potential of the counter electrode solution was determined to be ∼0.50 V versus SHE (measured by potentiometry using a Pt wire indicator electrode and a Ag/AgCl reference electrode). Because of the high concentrations of I^- and I_3^- in this solution, the redox potential is expected to remain practically unchanged during the RFEW experiments since oxidation of all BMPAP and I^- in the window and window compartment will cause a negligible change in I_3^- and I^- concentrations in the counter electrode side. Furthermore, because of the very high concentrations relative to the window compartment, charge transfer and diffusion overpotentials at this electrode are expected to be very small so that its potential should remain close to the solution redox potential even when current is flowing.

To switch the RFEW to a colored state the peristaltic pump was switched on, and a +0.50 V bias (window-side electrode vs counter electrode) was applied across the external cell, corresponding to ∼1 V electrode potential versus SHE in the

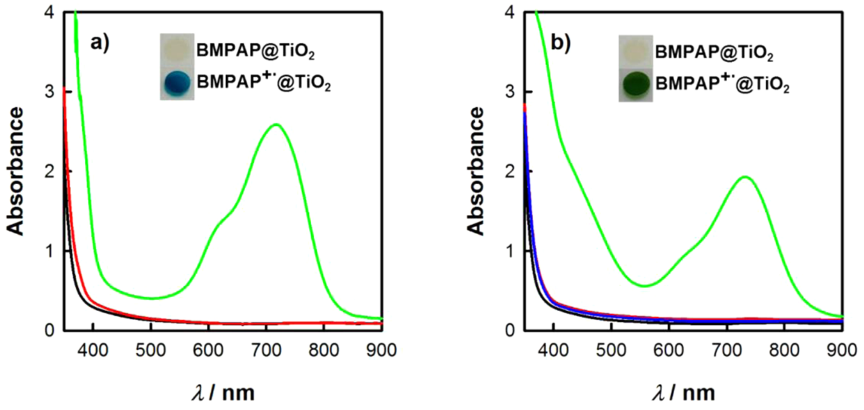

Figure 4. Absorbance spectra of BMPAP-coated mesoporous TiO_2 films. (a) Absorbance of BMPAP (red) and electrochemically produced BMPAP$^{+\cdot}$ (green) on a mesoporous TiO_2 (black) film. (b) Absorbance of a freshly prepared BMPAP/TiO_2 film (red), BMPAP$^{+\cdot}$ produced by I_3^-/I_2 oxidation (green), and BMPAP produced by reduction of BMPAP$^{+\cdot}$ by I^- (blue). (insets) Representative photographs of the films in decolored and colored states.

absence of Ohmic losses, which are significant due to milliampere currents and ∼100 Ω solution plus membrane resistance (estimated from the high-frequency cell impedance). To decolor the window a −0.50 V bias was applied, again with the pump running. These bias voltages were chosen to achieve a rapid rate of electrolysis of I^- or I_3^- while also avoiding production of higher-order polyiodides or evolution of oxygen or hydrogen gas at the electrodes.

Figure 5 shows representative photographs of the RFEW in fully decolored and colored states. A logo was placed directly behind the window to help indicate the color and transparency of the window. The colored state was achieved by applying +0.50 V to the window compartment electrode versus the counter electrode for approximately 2 min while pumping continuously. The decolored state could be recovered by reversing the bias voltage for ∼15 min or by pumping a 0.1 M KI solution through the window cavity for a few minutes. The relatively slow switching times compared to other reports of EC devices in the literature are partly ascribable to the large area of our prototype (∼40 cm^2 unblocked area compared to the more typical <1 cm^2 area in other EC device reports). Figure 6 shows the corresponding transmittance spectra of the window in decolored and colored states. The pump and bias voltages were switched off during measurement of the transmittance spectra.

Figure 5. Photographs of the redox-flow electrochromic window. (a) Decolored state and (b) colored state. A logo is placed behind the window to give an indication of the level of transparency and color.

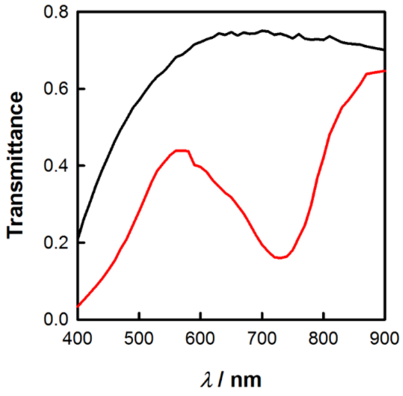

Figure 6. Transmittance spectra of the RFEW. The black curve shows the transmittance spectrum in the decolored state after application of a −0.50 V bias for 15 min, and the red curve shows the spectrum in the colored state after application of +0.50 V for ∼2 min. The trough centered at ∼730 nm and the decrease in transmission <550 nm are caused by the presence of BMPAP$^{+\cdot}$ on the TiO_2 films and I_3^- in the electrolyte solution, respectively.

Cycling Performance. Figure 7a shows a transmittance transient at 730 nm during continuous cycling between decolored and colored states. Figure 7b shows the corresponding current transient. One cycle consists of biasing the window compartment electrode to +0.50 V versus the counter electrode for 2 min, switching off the pump, and switching the cell to open circuit for 10 min, applying −0.50 V for 16 min, and finally switching off the pump and bias for another 10 min. The 2 and 16 min oxidation and reduction times are optimized to achieve almost full coloration and decoloration while maintaining good stability in each state. It was found that if an oxidizing bias is applied for much longer than 2 min the window begins to irreversibly lose coloration, presumably due to overoxidation of the BMPAP, although the exact mechanism has not yet been established (Supporting Information). However, as shown in Figure 7a, this undesirable phenomenon is avoided with a sufficiently short oxidation time. With optimized bias timings multiple cycles can be completed with reasonably good retention of transmittance in both colored and decolored states. The colored state was in fact observed to be stable for many hours after switching off the pump and bias, which is promising for practical applications. The relatively slow switching times of the present prototype exclude immediate application in displays or other situations where very rapid switching is required (e.g., car rearview mirrors), but architectural applications are feasible.

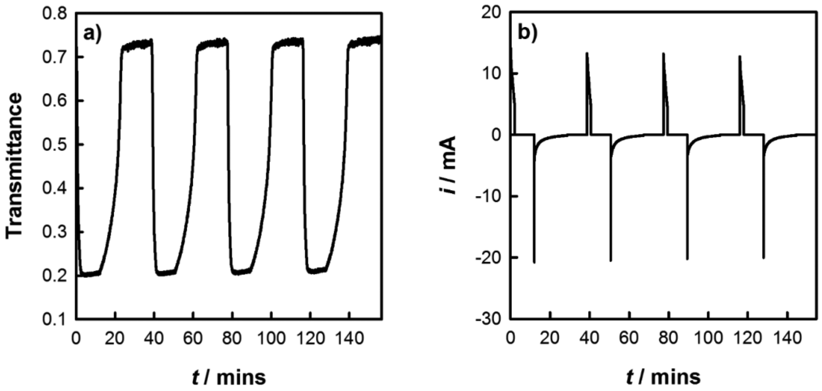

Figure 7. Cycling performance of the RFEW. (a) Transient transmittance at 730 nm and (b) the associated current transient for the RFEW during cycling between colored and colorless states. The colored state was induced by polarizing the carbon cloth electrode in the compartment connected to the window to +0.50 V vs the electrode in the other compartment for 2 min. The colorless state was recovered by reversing the polarity for 16 min. Note that almost constant transmittance is maintained in both colored and colorless states for 10 min periods between each application of bias voltage.

CONCLUSIONS

In summary, a novel EC window that utilizes a redox flow system to replace costly TCOs has been introduced and demonstrated for the first time. The RFEW design obviates the need for TCO substrates by utilizing redox targeting and flow cell concepts to remotely address the EC film within the window cavity. In its construction, the RFEW utilizes only nontoxic components that are relatively stable in the presence of water and oxygen, which should relax sealing requirements and improve long-term stability in eventual commercial applications. It might be argued that utilization of an expensive ion-selective membrane such as Nafion (commercially available for ~\$1800/m^2 at the time of writing) in the external two-compartment cell cancels any cost reduction due to removing the TCO. However, note that the area of ion-selective membrane required is much smaller than that of the glass. For example, in our prototype the area of Nafion employed was >80× smaller than the area of glass used (and could be reduced further if the switching voltage is increased to compensate for increased membrane resistance), yet commercially available Nafion is only ~6× more expensive than FTO-coated glass per m^2 at the time of writing.

The prototype RFEW employs a triphenylamine derivative (BMPAP) anchored to a mesoporous TiO_2 scaffold as its EC component. We find that BMPAP can be rapidly oxidized by aqueous I_3^- solution to form the colored BMPAP$^{+\bullet}$ radical cation, which can then be reduced back to colorless BMPAP by aqueous I^- solution. By electrochemically generating aqueous I_3^- or I^- in an external two-compartment cell and pumping the solution through the window cavity it is possible to reversibly cycle the RFEW between colored and colorless states. The prototype RFEW exhibits good transparency and a striking blue/green color in its colored state. Under suitable conditions, both colored and colorless states are stable and several coloration/decoloration cycles can be performed with minimal loss in performance.

Although more stringent coloration, stability, and switching time criteria will need to be satisfied for commercial applications, the present prototype is a very promising first attempt and neatly demonstrates the RFEW concept. A number of possible strategies for improving the performance of the RFEW exist. Different colors may be achieved by replacing the BMPAP with other electrochromes (e.g., phenoxazine for a red color) or by coadsorbing more than one electrochrome onto the same TiO_2 layer. Alternatively, inorganic or polymeric EC materials may be used to replace the mesoporous TiO_2 entirely. Switching times can be optimized by selecting a different redox mediator or by using a pair of redox mediators with redox potentials laying either side of the electrochrome potential to increase the driving force available for reduction and oxidation of the electrochrome.

ASSOCIATED CONTENT

Supporting Information

Transmission transients showing irreversible decoloration of the RFEW upon excessively long exposure to an oxidizing redox solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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