Photoelectrochromic windows and displays

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Photochromic materials change colour on absorption of light, whereas electrochromic materials change colour in response to an electrically induced change in oxidation state. Both classes of materials are being investigated for potential applications in displays, imaging devices and ‘smart’ windows. Here we describe an alternative route to such applications, in which an electrochromic film and a photovoltaic film form the two electrodes of an electrochemical cell. The resulting structure exhibits photochromism, but unlike conventional photochromic films, the light-absorption process (in the photovoltaic film) is separate from the colouration process (in the electrochromic film): both may therefore be optimized individually. Moreover, as the coloration process in our cells requires an external electrical current between the two electrodes, the optical state of the cell—transparent, absorbing or, in the case of non-uniform illumination, patterned—can be stored when the circuit is open, or changed when the electrodes are connected.

The light-absorbing function in the photoelectrochromic (PEC) cell is performed by a dye-sensitized semiconductor electrode that produces a photovoltage sufficient to colour the electrochromic film deposited on the counter electrode. Dye-sensitization has a long history of use in colour photography and is currently being studied as a potential means of solar energy conversion. Some of the best-known electrochromic materials are inorganic oxides such as WO₃ and MoO₃. We illustrate the principle of the photoelectrochromic cells with a ruthenium polypyridine-sensitized nanocrystalline TiO₂ electrode, similar to those introduced by Grätzel et al. for use in solar cells, and a WO₃ electrochromic film on the counter electrode.

The dye, Ru(n)₂L', where L is 2,2'-bipyridine-4,4'-dicarboxylate and L' is 4,4'-dimethyl-2,2'-bipyridine, was adsorbed onto 4-μm-thick nanocrystalline TiO₂ films from dilute (8 μM) ethanol solution containing 30 mM chenodeoxycholic acid. The dye coverage was kept low to make the cells almost transparent in the ‘off’ state; the coadsorbate, chenodeoxycholic acid, was used to

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The sensitization process produces a photovoltaic current, which can be used to drive a battery. The dye-sensitized electrode is charged to its bleached state. If the electrodes are opened before the incident light is blocked, the cell remains coloured because the electrons cannot escape from the reduced WO₃ film.

Photographs of a 25-cm² cell in bleached, coloured and inhomogeneously coloured states are shown in Fig. 2. When the electrolyte layer is thin (~25 µm in our examples) compared to the size of the cell, spatially resolved coloration occurs when just part of the cell is illuminated. Lateral mobility in the electrolyte limits the spatial resolution of the device; however, once the Li ions are intercalated into the WO₃ film, their lateral mobility becomes so small that an image can be stored for many hours. Figure 2c shows an example where only part of the device was illuminated. The unexposed part remained transparent whereas the illuminated part became coloured. The pattern was still visible after storage of the device with open-circuit terminals for more than 24 h. The rate of colouring and bleaching of a cell on exposure to chopped white light of ~75 mW cm⁻² intensity was probed by measuring the transmission of a weak laser beam at 788 nm wavelength (Fig. 3). On illumination, the transmission decreased to its saturation level after ~100 s.

If one corner of the PEC cell is darkened by short-circuiting the electrodes, this voltage is sufficient to drive a battery. The colour is dark blue. The inhomogeneously coloured state achieved by illumination at one corner of the cell, issuing from the sensitizing dye and some scattering from the TiO₂ electrode, is shown in Fig. 1.

Light absorption by the sensitizing dye leads to electron injection into the TiO₂ film, with aqueous yield at short circuit of ~70%. This is followed by re-reduction of the oxidized dye via electron transfer from the TiO₂ electrode. The tungsten bronze (Li₂WO₃) that is responsible for most of the absorbance in the coloured state has a broad absorption maximum around 1,000 nm.

The electrochromic process is highly reversible and lifetimes of over 10⁷ cycles have been achieved in display applications. The colouring process is equivalent to charging a battery; the photovoltage generated by the dye-sensitized electrode is used to drive Li⁺ ions and electrons into the WO₃ film. When the light is blocked after the WO₃ electrode is charged, a voltage equal to the open circuit photovoltage, but of opposite polarity, appears across the PEC cell. If the electrodes are then short-circuited, this voltage causes the cell to discharge spontaneously back to its bleached state.
electrodes. In the latter case, the device would be transparent to visible light in the 'off' state but could be darkened by sunlight or addressed with an infrared diode laser. Perhaps most importantly, the dye-sensitized electrodes are inexpensive, robust and can be easily scaled up to give large-area substrates.

FIG. 3 Change in transmission at 788 nm wavelength of a short-circuited PEC cell exposed to chopped white light.

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