Supporting information

Perovskite photovoltachromic cells for building integration

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**Molybdenum trioxide and titanium dioxide electrochromic devices**

We prepared additional electrochromic devices using molybdenum trioxide and titanium dioxide as electrochromic films and we compared their electrochromic properties to those we collected for tungsten trioxide based devices. Molybdenum trioxide and titanium dioxide films were prepared using the same physical vapour deposition technique described in the Experimental Section for tungsten trioxide and all of them have been prepared with the same thickness (about 350nm) to compare their optical properties. Devices prepared with different metal oxides were assembled following the procedure described in the Experimental section for tungsten trioxide based devices.

![Graph showing transmittance spectra](image)

**Figure S1 – Transmittance spectra of bleached (0.6V) and colored (-0.7V) devices containing a WO$_3$ electrochromic film. Inset: WO$_3$ device in coloured and bleached conditions.**

In Figure S1 we reported the transmittance spectra of the electrochromic device prepared with tungsten trioxide (WO$_3$). As described in the main text, WO$_3$ enabled relatively high transmittance in bleached conditions and optical modulation of about 25% at wavelength of 600 nm. Such modulation was obtained applying a bias of 0.7 V, which is perfectly compatible with the photovoltaic output of the semi-transparent perovskite solar cell prepared for this work.
In Figure S2 we reported the transmittance spectra of the electrochromic device prepared with titanium dioxide (TiO$_2$). We tested the optical modulation under a wide range of voltages. However, we found that a significant modulation can be observed only when a voltage higher than 2V was applied. Therefore, a single semi-transparent perovskite solar cell is not sufficient to power an electrochromic devices made with TiO$_2$.

Figure S2 – Transmittance spectra of bleached (0.7V) and colored (-2.2V) devices containing a TiO$_2$ electrochromic film. Inset: TiO$_2$ device in coloured and bleached conditions.

In Figure S3 we report the transmittance spectra of the electrochromic device prepared with molybdenum trioxide (MoO$_3$). We tested the optical modulation under a wide range of voltages. However, we found that a significant modulation can be observed only when a voltage higher than 2V was applied. Therefore, a single semi-transparent perovskite solar cell is not sufficient to power an electrochromic devices made with MoO$_3$.

Figure S3 – Transmittance spectra of bleached (1.6V) and colored (-0.7V) devices containing a MoO$_3$ electrochromic film. Inset: MoO$_3$ device in coloured and bleached conditions.
In Figure S3 we reported the transmittance spectra of the electrochromic device prepared with molybdenum trioxide (MoO$_3$). A relatively large modulation of about 25% was measured with a bias voltage of 2.2V. Therefore, similar to what we found for the TiO$_2$ based electrochromic device, a single semi-transparent perovskite solar cell cannot deliver the voltage necessary to drive the colouration.
**Electrolyte and device stability**

We performed chronoamperometric measurement with over $10^4$ charge/ discharge cycles (see Figure S4). We measured the ionic conductivity before and after $10^4$ charge/ discharge cycles of the electrochromic device. We observed a decrease in ionic conductivity from the initial value of $1.25 \times 10^{-5}$ S cm$^{-1}$ to a final value of $1.40 \times 10^{-6}$ S cm$^{-1}$ and a decrease in the injected charge density from 2.4 mC/cm$^2$ to 1.2 mC/cm$^2$. This value is consistent with literature [C.M. Lampert, Proceeding SPIE Volume 1272, Optical Material Technology for Energy Efficiency and Solar Energy Conversion IX, The Hague, The Netherlands 1990] where a drop from 6 mC/cm$^2$ to 1 mC/cm$^2$ has been reported after $10^5$ cycles. Such performance decay after $10^4$ cycles could be correlated to the lower ionic conductivity of the electrolyte and the increase sheet resistance of the ITO electrodes in contact with acidic electrolytes.

![Figure S4 – Comparison between charge and discharge curves obtained in as prepared device and in the same device after $10^4$ cycles.](image)

The reduction of charge absorption will induce decreasing of transparency modulation, which we reported in in Figure S5.
Figure S5 - Decrease of optical modulation after $10^4$ cycles of colouring and bleaching.

More detailed studies of the degradation mechanisms and the long-term stability are currently under investigation and they will be published elsewhere.
Coloration mechanism

Figure S6. Cross-section of the device reporting a schematic description of the coloration mechanism, which is activated by the voltage generated in the photovoltaic device.