Supporting Information

High-Contrast Switching of Plasmonic Structural Colors: Inorganic vs Organic Electrochromism

Marika Gugole,1‡ Oliver Olsson,1‡ Kunli Xiong,1 Jolie C. Blake,1 José Montero Amenedo,2 Ilknur Bayrak Pehlivan,2 Gunnar A. Niklasson2 and Andreas Dahlin,1*

1 Department of Chemistry and Chemical Engineering, Chalmers University of Technology, 41296 Gothenburg, Sweden.

2 Department of Materials Science and Engineering, Uppsala University, P.O. Box 534, SE-75121 Uppsala, Sweden.

‡ These authors contributed equally.

* Corresponding author adahlin@chalmers.se

Content:

Description of videos, figures S1-S8. Total 8 pages.
Description of videos (merged into one .avi file) included as supporting online material:

Green_PProDOTMe2_Spot: Switching a green sample with polymer in real-time. A reduced illumination spot is used (constant intensity).

Green_WO3_Spot: Switching a green sample with inorganic film in real-time. A reduced illumination spot is used (constant intensity).

Red_WO3: Switching a red sample with inorganic film in real-time. The illuminated region is ~1 mm wide. Note that the intensity is not homogenous here.

Blue_Stripes_PProDOTMe2: Selectively switching the blue stripes with polymer in real-time.

Green_Stripes_Cell: The green stripes on a region of the sample are being switched. A whole flow cell with electrodes is shown.
Figure S1 Calculated surface plasmon dispersion relation in the thin film multilayers. The refractive index of Al₂O₃ was set to 1.8, which gave excellent agreement between Fresnel simulations and experimental reflectivity, and the thickness to 100 nm. The characteristic spacing between the colloids used gives a quasi-periodicity slightly below 300 nm, for which coupling is predicted at 700 nm. This is in agreement with the red-yellow scattering observed on green-blue samples. The field plot is generated at 700 nm. As expected, the plasmonic field is partly localized at the Al-Al₂O₃ interface.
Figure S2 The left picture shows samples prepared by other electrochemical methods, illustrating that it is not straightforward to create uniform films by electropolymerization. (1) Cyclic voltammetry 10× [1.5 V; −0.3 V] 100 mV/s, (2) Constant current [80 µA] 150 s, (3) Cyclic voltammetry 10× [1.5 V; −0.3 V] 100 mV/s, (4) Cyclic voltammetry on ITO (no polymer formed), (5) Cyclic voltammetry 28× [1.5 V; −0.3 V] 100 mV/s, (6) Cyclic voltammetry 3× [1.5 V; −0.3 V] 100 mV/s, (7) Constant potential [1.1 V then 1.2 V], (8) Constant current [40 µA then 80 µA], (9) Pulsed deposition [1.8 V 0.5 s; −0.3 V 0.5 s]. Note that these voltages were vs Ag/AgCl and another cell was used (which also influences quality and reproducibility). For comparison, the right image shows films of different thickness prepared by the optimized recipe.
Figure S3 Thickness measured by profilometer of different electropolymerized films.

Figure S4 X-ray photoelectron spectroscopy analysis of a WO₃ film prepared by reactive sputtering. Comparing the signal from the O1s and the W4f peaks gave a stoichiometry of O:W of 2.97 (which we refer to as WO₃).
The film was deposited on a glass slide where the other side was coloured black to avoid reflection. The thickness was allowed to vary and was fitted to 47.8 nm. Note that $n$ is above 2, which gives rise to interference peaks in the visible already for relatively thin films. Note also that this film may be a little bit less absorbing than the “bright” state of WO$_3$ in experiments because it has never been exposed to Li$^+$. The $k$ values in the literature data were ~50% higher, although $n$ was identical (within measurement error). Hence, these data were not used to simulate WO$_3$ in its bright state but serve as a verification that our films have very similar optical properties to those presented in literature.

**Figure S5** Determination of as deposited WO$_3$ film permittivity by spectroscopic ellipsometry.
**Figure S6** Simulated reflectivity of metasurfaces when WO$_3$ and electrolyte is introduced on top. The WO$_3$ is in its bright state. The dashed lines are simulations of the same structure without the WO$_3$ and in air ($n = 1$). These simulations do not take the nanoholes into account, which makes them inaccurate in the red region for blue and green samples as expected (compare with spectra in main text). However, the results work very well for describing the reflectivity maximum from the cavity resonance, which is sufficient for the purpose of finding a WO$_3$ film thickness that does not alter the color significantly. Simulations were performed as in previous work (see main text) and their accuracy is verified below.

**Figure S7** Comparing simulations and experiments for a red sample with WO$_3$ in bright and dark states. The electrolyte is represented with refractive index 1.42. The simulated absolute reflectivity values are generally a bit shifted to higher values in the red region. Overall the agreement is considered to be satisfactory.
Figure S8 Cross-section electron microscopy images of relatively thick electrochromic films. The porosity of WO$_3$ cannot be visualized since the pores are expected to be very small. For the polymer, the images indicate a highly porous soft network.