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ISE 2010 Symposium 5: Electroactive Polymers, Inorganic Electroactive Solids, Nanocomposite Materials

Synthesis, electrochromism and display-device applications of electroactive Ruthenium Purple films prepared by ‘directed assembly’ and electrochemical precipitation techniques

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Aim and objectives

• **Aim:** to fabricate thin-layer electrochromic devices and to quantify colour changes

• **Objectives:**
  - to prepare stable films of the inorganic electroactive solid Ruthenium Purple (RP)
  - to pair with viologens in the fabrication of colour-reinforcing electrochromic devices
  - to quantify the colour stimulus of the individual electrochromic materials and the electrochromic devices
Structure of presentation

1. Background to Ruthenium Purple (RP)
2. Directed assembly of RP
3. Electrochemical precipitation of RP and spectroelectrochemistry
4. Quantification of colour stimuli – colorimetry of RP and viologen systems
5. Thin-layer electrochromic devices
Ruthenium Purple (RP)

- general formula of metal hexacyanometallates:
  - $M_x^A[M^B(CN)_6]^y$ (x, y integral)
- the $M^B$ metal ions are coordinated in a strong cyanide ligand field and are low spin
- the $M^A$ metal ions are coordinated in a weak nitrile ligand field and are high spin
- in RP the two transition metals in the formula are $\text{Ru}^{II}$ (bonded to C) and $\text{Fe}^{III}$ (bonded to N)
- exhibits a broad $\text{Ru}^{II} – \text{Fe}^{III}$ IVCT band
Directed assembly of RP

- adsorb iron(III)cations then hexacyanoruthenate(II) anions
Electrochemical precipitation of RP

• synthesised by an electrochemical coagulation technique using an aqueous nanoparticulate RP colloidal suspension prepared from separate very dilute aqueous solutions of iron(III) chloride and potassium hexacyanoruthenate(II), with dilute potassium chloride as supporting electrolyte solution. To aid stability of the RP films, ruthenium(III) chloride was added to the RP colloidal suspension.
RP precipitation
RP precipitation and spectroelectrochemistry
Colorimetry

- **Luminance** – the brightness of the colour … with one value, luminance provides information about the perceived transparency of a sample over the entire visible range.

- **Hue** – identifies a colour by its location in the spectral sequence … red, yellow, green, blue …. dominant wavelength associated with the colour, where maximum contrast occurs.

- **Saturation** – the level of white and/or black … vivid colours, dull colours …. (*chroma, tone, intensity, or purity*)
CIE 1931 colour space

- CIE System of Colorimetry
  (Commission Internationale de l’Eclairage)
- 3 attributes of colour: Luminance, Hue, Saturation
- Colour matching functions \( \Rightarrow \) tristimulus values (XYZ)
\( \rho(\lambda) \)  
Ideal spectrum

\( \rho(\lambda), S(\lambda) \)

\( (\rho(\lambda) \cdot S(\lambda)) \)

\( \phi(\lambda) \)  
Actual spectrum

\[
\text{normalize } \left( \frac{\phi(\lambda)}{\sum_0^{\infty} \phi(\lambda) \, d\lambda} \right)
\]

\( I(\lambda) \)

\[
\text{numerical integration } \left( \int I(\lambda) \, \bar{x}(\lambda) \, d\lambda \right)
\]

\( \bar{x}, \bar{y}, \bar{z} \)  
Colour-matching functions

\( X, Y, Z \)  
Tristimulus values

\[
\text{normalize } \left( x = \frac{X}{X + Y + Z} \right)
\]

\[
\text{normalize } Y_L = \frac{Y}{Y_0}
\]

\( x, y, z \)  
Chromaticity coordinates

\( xyY \)  
Chromaticity coordinates

\( S(\lambda) \)  
Non-ideal light source
RP colour switching and colorimetry
Methyl viologen spectroelectrochemistry

Reduction

Re-oxidation

A / a.u.

λ / nm

300 400 500 600 700

0.25

0.20

0.15

0.10

0.05

0.00

0.45

0.40

0.35

0.30

0.25

0.20

0.15

0.10

0.05

0.00

300 400 500 600 700

λ / nm

0.25
Methyl viologen colour switching and colorimetry (I)

Graphs showing the relationship between $E/V$ and $I/\mu A$ for the first graph, $Q/\mu C$ for the second graph, and $Y_L(\%)$ for the third graph.
Methyl viologen colour switching and colorimetry (II)
Heptyl viologen spectroelectrochemistry

Reduction

Re-oxidation

A / a.u.

λ / nm
Heptyl viologen colour switching and colorimetry (I)
Heptyl viologen colour switching and colorimetry (II)
Thin-layer electrochromic device fabrication

(a) Etched ITO electrode  
(b) Coated etched electrode

(c) Attached Teflon spacers  
(d) Final device

Metal Hexacyanometallate

Glass

ITO

Solution
RP/10 mM methyl viologen device (I)
RP/10 mM methyl viologen device (II)
RP/10 mM heptyl viologen device (I)
RP/10 mM heptyl viologen device (II)

(a) Colourless

(b) Coloured

(c) $\lambda_c = 555 \text{ nm}$

(d) Colourless

Coloured
Summary

• The electroactive inorganic solid Ruthenium Purple has been paired with methyl and heptyl viologens in colour-reinforcing thin-layer electrochromic devices
• The colour stimuli of the individual electrochromic materials and the devices have been quantified by transformation of absorption spectra recorded during colour switching
• The colour measurement and device fabrication methods will be applicable to other electrochromic materials