



Synthesis, characterisation and *in situ* colorimetry of electrochromic Ruthenium purple thin films

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ABSTRACT

Ruthenium purple (RP) films on transmissive tin-doped indium oxide (ITO)/glass substrates have been synthesised by an electrochemical coagulation technique using an aqueous 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. Using the CIE (Commission Internationale de l'Eclairage) system of colorimetry, the colour stimulus of the electrochromic RP films and the changes that take place on reversibly switching to the colourless form have been calculated from *in situ* visible spectra recorded under electrochemical control. On electrochemical reduction, the intensely absorbing bright purple mixed-valence iron(III) hexacyanoruthenate(II) chromophore is reduced to the colourless iron(II) hexacyanoruthenate(II) form. Sharp and reversible changes in the hue and saturation occur, as shown by the track of the CIE 1931 *xy* chromaticity coordinates. Concurrently, as the purple chromophore is bleached, a large increase in the relative luminance of the electrochromic film is observed. For the purple state, the CIELAB 1976 colour space coordinates were $L^* = 64$, $a^* = 27$ and $b^* = -36$, with a complementary wavelength (λ_c) calculated as 555 nm, in excellent agreement with the absorption maximum (λ_{max}) of 550 nm for the intervalence charge-transfer (IVCT) band.

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1. Introduction

Prussian blue (PB), the earliest [1] modern synthetic pigment (C.I. Pigment Blue 27), has an extensive history of use in the formulation of paints, lacquers, printing inks, typewriter ribbons and carbon paper [2–4]. The intense colour of the iron(III) hexacyanoferrate(II) chromophore arises from intervalence charge-transfer (IVCT) between the mixed-valence iron oxidation states [5]. PB and numerous other polynuclear metal hexacyanomethylates [6], can be deposited onto inert electrode substrates to give redox-active films that have electrochromic properties [7,8]. We have earlier described the application of an *in situ* colorimetric method, based on the CIE (Commission Internationale de l'Eclairage) system of colorimetry, to the study of electrochromism in PB films [9]. We now report the quantification of the colour stimulus in films of the Group 8 PB analogue, Ruthenium purple (RP), and the changes that take place on reversibly switching the intensely absorbing bright purple iron(III) hexacyanoruthenate(II) chromophore to the colourless form, iron(II) hexacyanoruthenate(II).

Although thin-film PB is readily available through electrochemical reduction of solutions containing iron(III) and hexacyanoferrate(III) ions [6–9], synthesis of RP films [10–19] is less straightforward. Salts of the analogous hexacyanoruthenate(III) ion are not commercially available, and although preparation by chemical or electrochemical oxidation of hexacyanoruthenate(II) is possible, the resulting solution is unstable. In the synthetic procedure described here, we employ an electrochemical coagulation technique using an aqueous RP colloidal suspension prepared from separate fresh very dilute solutions of iron(III) chloride and potassium hexacyanoruthenate(II), with dilute potassium chloride as supporting electrolyte. This technique was first introduced by Cataldi et al. [12] and here we provide an explanation of the need to adhere to specific concentrations for reproducible success in RP film formation and give exact synthetic details for the preparation and use of the colloidal suspension.

2. Experimental

2.1. Materials

Working electrode substrates were tin-doped indium oxide (ITO) on glass (7 × 50 × 0.7 mm, 5–15 Ω/□, part no. CG-50IN-CUV)

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from Delta Technologies Limited. Before each RP film formation, ITO/glass substrates were pre-treated, in order to remove any trace of adhesive/impurities on the surface, by sonication (5 min) in isopropyl alcohol followed by rinsing with deionised water and air drying. The counter electrode was platinum gauze and the reference electrode was Ag/AgCl (3.0 mol dm^{-3} NaCl). Anhydrous iron(III) chloride, potassium hexacyanoruthenate(II) hydrate, ruthenium(III) chloride, potassium chloride and hydrochloric acid (all Sigma–Aldrich) were of the highest purity available and used without further purification. All deionised water for solution preparation and the resulting electrolyte solutions and colloidal suspensions were deoxygenated by nitrogen purging for 20 min prior to all measurements.

2.2. Electrochemical and spectroelectrochemical measurements

An ECO Chemie Autolab PGSTAT 20 potentiostat was used for electrode potential control, with *in situ* visible region spectra being recorded using a Hewlett Packard 8452A diode array spectrophotometer. A single-compartment glass electrochemical cell was used for electrochemical deposition and cyclic voltammetric characterisation of RP films. For *in situ* spectroelectrochemistry, a 1 cm pathlength plastic cuvette was used, with a machined polytetrafluoroethylene lid that allowed the ITO/glass working electrode to be mounted parallel to the optical faces. Additional holes in the lid allowed for the counter and reference electrodes to be positioned in the electrolyte solution, and nitrogen purging prior to measurements. The lower 4 cm of each ITO/glass substrate was immersed in solution, providing a submerged geometric electrode active area of 2.80 cm^2 . Adhesive copper tape at the top of each ITO/glass substrate provided the means for a uniform electrical contact. In the computation of CIE 1931 chromaticity coordinates, the spectral power distribution of the D_{55} light source was used.

2.3. Crystallographic and morphological studies

Powder X-ray diffraction (XRD) analysis of RP films on ITO/glass substrates was carried out with a Bruker D8 Advance diffractometer, using monochromatic CuK α_1 radiation at $\lambda = 1.5406 \text{ \AA}$ and a position sensitive detector (PSD). Perspex flat plate sample holders were used to mount the samples and data were collected between the 2θ range of $5\text{--}90^\circ$, using 0.014767° steps over a period of 4 h.

Scanning electron micrographs (SEM) were produced on a Carl Zeiss 1530 VP Field Emission Gun Scanning Electron Microscope (FEG-SEM) with an EDAX Phoenix energy dispersive X-ray microanalysis system.

A Malvern Zetamaster ZEM5002 colloid analyser was used to determine the particle size distribution of colloidal RP present in the deposition solution. The instrument was calibrated using Nanosphere™ size standards ($220 \pm 6 \text{ nm}$), which gave a mean measurement of 220.7 nm (over ten measurements). The zeta potential of the deposition solution was measured using the same instrument and calibrated using a zeta potential transfer standard ($-50 \pm 5 \text{ mV}$), which gave a mean reading of 52.3 mV (over ten measurements).

2.4. Preparation of a dilute colloidal suspension of Ruthenium purple

An aqueous solution of 1 mmol dm^{-3} potassium hexacyanoruthenate(II) was first prepared by dissolution of potassium hexacyanoruthenate(II) hydrate powder in deoxygenated water (25 cm^3) that contained 35 mmol dm^{-3} potassium chloride. A separate aqueous solution containing 1 mmol dm^{-3} iron(III) chloride

was next prepared by dissolution of high purity ($>99.99\%$) anhydrous iron(III) chloride powder in deoxygenated water (25 cm^3) that contained 35 mmol dm^{-3} potassium chloride. The two freshly prepared solutions were then rapidly mixed with vigorous stirring to yield a brilliant-purple opaque RP dilute colloidal suspension, which was then adjusted to pH 2 by the addition of hydrochloric acid. Under ultrasonic agitation and further nitrogen purging, 1 cm^3 of a 1 mmol dm^{-3} aqueous ruthenium(III) chloride solution was added to the suspension by pipette, to give $0.02 \text{ mmol dm}^{-3}$ ruthenium(III) chloride. It was essential to use the RP dilute colloidal suspension within *circa* four hours, after which time particles start to irreversibly coagulate and collect at the bottom of the container.

3. Results and discussion

3.1. Reproducible synthesis and characterisation of Ruthenium purple films

RP films on ITO/glass were synthesised by adaptation of a literature method [12]. Using the procedure described above (section 2.4), RP was first prepared as a dilute colloidal suspension by mixing separate aqueous solutions containing low concentrations of equimolar iron(III) chloride and potassium hexacyanoruthenate(II) in potassium chloride supporting electrolyte. On mixing of the reagent solutions, water molecules coordinated to the Fe^{III} ions are displaced by nitrogen atoms from the hexacyanoruthenate(II) ions to generate an extended RP framework based on a face-centred cubic unit cell with $\text{Fe}^{\text{III}}\text{--CN--Ru}^{\text{II}}$ bridges [20,21]. Under the described experimental conditions, the dilute RP colloidal suspension had a uniform particle size distribution (Fig. 1) with a mean particle size of 8.3 nm , and remained below the critical coagulation concentration (CCC) for up to four hours. The mean zeta potential value of -22.81 mV (over ten measurements) was indicative of the incipient instability of the dilute RP colloidal suspension.

To achieve reproducible RP films it was essential to exactly follow the procedure detailed above, which was established following extensive explorative work. If not exactly followed, synthesised RP films are often non-adherent, and irreproducible cyclic voltammograms are obtained during RP film growth and subsequent redox cycling. Preparation of separate dilute reagent solutions, followed by rapid mixing with vigorous stirring was essential and prevented further growth of nuclei and irreversible bulk coagulation. To allow continuous RP film growth, the supporting

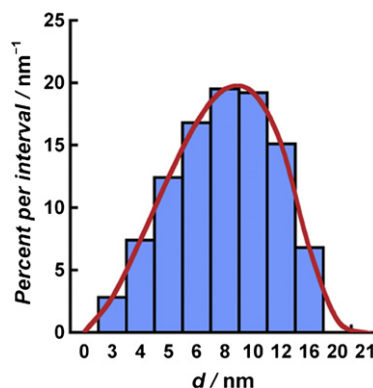


Fig. 1. Particle size distribution, measured using a Malvern Zetamaster ZEM5002 colloid analyser, of a dilute colloidal suspension of RP formulated from an aqueous solution containing potassium hexacyanoruthenate(II) (0.5 mmol dm^{-3}), iron(III) chloride (0.5 mmol dm^{-3}), potassium chloride (35 mmol dm^{-3}), and ruthenium(III) chloride ($0.020 \text{ mmol dm}^{-3}$) set at pH 2 with hydrochloric acid.

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