High contrast solid state electrochromic devices based on Ruthenium Purple nanocomposites fabricated by layer-by-layer assembly†

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Received (in Cambridge, UK) 6th March 2008, Accepted 6th May 2008
First published as an Advance Article on the web 12th June 2008
DOI: 10.1039/b803915a

Electrochromic Ruthenium Purple–polymer nanocomposite films, fabricated by multilayer assembly, were found to exhibit sub-second switching speed and the highest electrochromic contrast reported to date for any inorganic material.

In the last two decades, the only inorganic non-oxide materials that have attracted significant attention for incorporation in low power electrochromic displays are those belonging to the metal hexacyanoferrate (HCNF) family.[1] In the HCNF family, Prussian Blue (PB) is by far the most studied electrochromic material. In contrast, Ruthenium Purple (RuP) has not been explored for electrochromic displays because the neutral form is insoluble in aqueous solution. Though nanocomposites incorporating polymer and inorganic materials have shown improved performance as compared to the separate constituents in terms of mechanical stability, electrochemical activity, and solar energy conversion,[2] their use in electrochromic devices has not been well studied. In this paper, we describe the synthesis of stable Ruthenium Purple nanoparticles and the electrochromic and surface properties of Ruthenium Purple–polymer nanocomposites fabricated by the layer-by-layer (LbL) assembly approach.

RuP belongs to the class of well-defined zeolite-like polynuclear inorganic materials with fixed metal ionic redox centers (*e.g.*, Ru(II) and Fe(III)) wherein the electroneutrality is maintained during the redox process by the movement of freely diffusing cations in and out of the lattice structure.[3] As discussed by several groups and similar to PB, RuP is present in two forms: ionized water-soluble $KFe^{III}[Ru^{II}(CN)_6]\cdot xH_2O$ and a neutral insoluble compound, $Fe^{III}_4[Ru^{II}(CN)_6]_3$.[4–7] The soluble RuP is present in a colloidal form and the inclusion of potassium makes it stable in aqueous media, bringing an overall negative charge, which allows LbL assembly using RuP colloids as the anions. As explained by Rosseinsky *et al.*,[8] the incorporation of K^+ as a 'supernumerary' cation in $Fe^{III}[Ru^{II}(CN)_6]$ makes it water-soluble. RuP ($Fe^{III}_4[Ru^{II}(CN)_6]_3/KFe^{III}[Ru^{II}(CN)_6]\cdot xH_2O$) in its natural form has a deep purple color and changes to colorless Ruthenium White (RW), $Fe^{II}_3[Ru^{II}(CN)_6]_2$ upon reduction. For the present studies, synthesis of 5 mM solution of RuP was carried out by mixing equal concentrations of potassium ruthenium cyanide ($K_4[Ru(CN)_6]$), ferric chloride ($FeCl_3$) and potassium chloride (KCl). KCl is added to ensure the excess of potassium ions crucial for the solubility of RuP. This was further purified by ultrafiltration to remove insoluble RuP, following the procedure described by DeLongchamp *et al.*[7] The composition of the as-synthesized product in powder form was confirmed by the X-ray diffraction (XRD) pattern (Fig. 1). The main peaks at 16.9° (200), 23.8° (220), 34.1° (400), 38.2° (420), and 44.3° (420) can be readily indexed as a pure face-centered cubic (fcc) phase of RuP [space group: *Fm*3*m*]. The broadening of the XRD is known to occur when the particle size reduces progressively below 200 nm.[9] The values are in good agreement with values reported by other groups for RuP and its analogs.[6,10,11]

Transmission electron microscopy (TEM) (Fig. 2) and dynamic light scattering (DLS) (see ESI Fig. S2(a)†) of the sample were taken from the diluted RuP solution and both techniques show that the average RuP nanoparticle size is 20–30 nm, which is in the range of values reported for HCNF nanoparticles by other groups.[7,12] RuP possesses a simple fcc lattice structure;[13,14] the metal ion centers in the fcc structure are Ru(II) and Fe(III) with cyanide groups between these ions. The presence of (200) fcc structure is confirmed by a fast

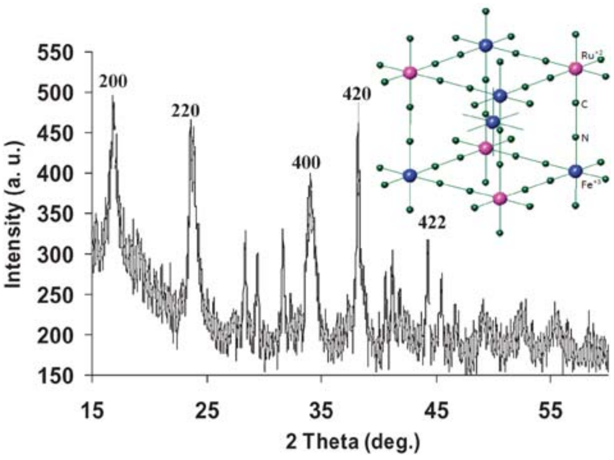

Fig. 1 An XRD pattern of the powder form of the RuP sample, confirming the formation of pure fcc $Fe_4[Ru(CN)_6]_3$. The inset is the unit cell of $Fe_4[Ru(CN)_6]_3$.

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† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/b803915a

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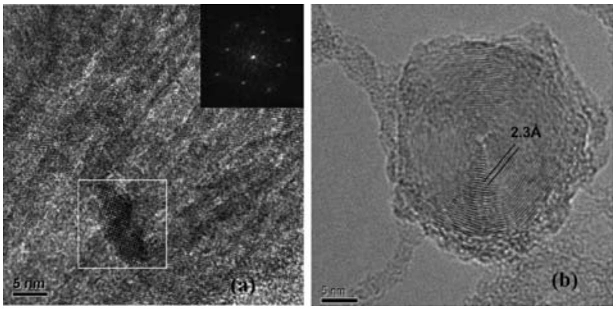

Fig. 2 TEM image (a) of the nanoparticles and FFT diffraction pattern (inset) of one of the marked nanoparticles; (b) shows the *d*-spacing values.

Fourier transform (FFT) image (inset of Fig. 2(a)) of the TEM diffraction pattern and is in agreement with the XRD results. The *d*-spacing value of 2.3 Å measured by TEM (Fig. 2(b)) for a crystal lattice (420) within the RuP nanoparticles with a lattice constant, $a = 10.26$ Å is in good agreement with the standard values for bulk cubic RuP.[15] Zeta potential measurements (see ESI Fig. S2(b)†) also confirmed the presence of two kinds of hexacyanoferrates, one of higher content ($>90\%$) with a negative potential value of −30.0 mV and the other low content insoluble part ($<10\%$) of value 2.5 mV. The amount of negative charge carried by soluble RuP nanoparticles is sufficient to fabricate films by LbL assembly. Though the colloidal dispersion of RuP nanoparticles is stable for months, sonication for 15–20 min before deposition results in better films due to breaking of the agglomerates.

Although the LbL approach has been used in the formation of (all-inorganic) PB and RuP multilayers on electrode surfaces,[6] the application of this technique in the production of hybrid polymer–inorganic nanocomposite films has so far been reported only for PB combined with either linear polyethylene imine (LPEI)[7] or polyaniline (PANI)[16] as the polymeric materials, but none has been reported for RuP. Herein, we show for the first time an adaptation of this approach to the formation of LPEI–RuP nanocomposite multilayered films with improved electrochromic properties. The LbL assembly approach introduced by Decher *et al.*[17] provides nanoscale control of multilayer film thickness. For LbL assembly, indium tin oxide (ITO) coated glass substrates were alternately immersed in 10 mM solution of LPEI at pH 4 and 5 mM solution of RuP at pH 4. Further details are provided in ESI.†

X-Ray photoelectron spectroscopy data (see ESI Fig. S3†) of the 40-bilayer LbL film (with an outermost layer of the film of RuP nanoparticles) of LPEI–RuP further showed almost 1 : 1 atomic concentration of Ru and Fe, confirming the presence of soluble RuP nanoparticles in the films, while higher ratios of Ru to Fe would have indicated the presence of extra Ru(II) occupying interstitial K^+ cationic sites in $[Ru^{II}(CN)_6]^{4-}$ lattice vacancies and making it insoluble. Spectroelectrochemistry studies of the RuP nanocomposite films in solution show the color change from purple–violet color to transparent as a negative voltage is applied. The absorption spectra from +1 V to −1 V, in 0.1 V steps, of a 40-bilayer film of LPEI–RuP nanocomposite are presented in Fig. 3. An exceptionally large change in transmittance of greater than 84% at a wavelength of 560 nm is observed as the film becomes transparent (RW) from the purple–magenta color (RuP). This is, to our knowledge, the highest contrast reported to date for any inorganic electrochromic material. The contrast values reported by DeLongchamp *et al.* are 77% (60 bilayers) and 61% (30 bilayers) for LPEI–PB[7] and PANI–PB,[16] respectively. There is no report of coloration efficiency or solid-state switching measurements in those publications.

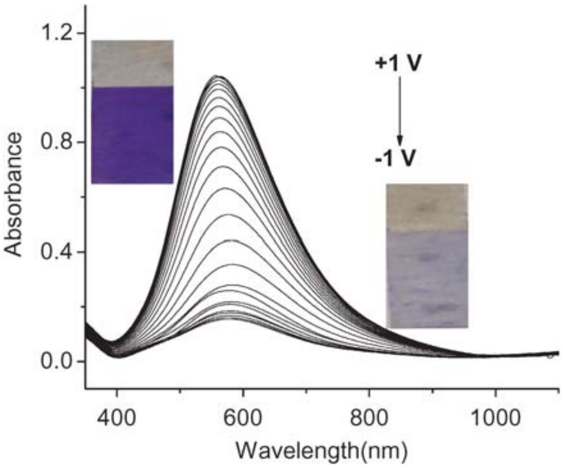

Fig. 3 Spectroelectrochemistry data of the absorbance of a 40-bilayer RuP film in 0.1 M $LiClO_4$–ACN solution on increase of voltage from +1 V to −1 V in 0.1 V steps.

Cyclic voltammetry (CV) was performed on the LPEI–RuP nanocomposite between −0.5 V to 1.0 V, which is the potential range expected for the RuP to RW transition (see ESI Fig. S4†). LPEI is an inactive polyelectrolyte, so the RuP controls the electrochemistry of the nanocomposite as confirmed by the agreement with the redox potential values of RuP found by other groups.[18] The reduction peak for RuP to RW was observed at 0.05 V which is in agreement with the reported values.[5,7] The corresponding oxidation peak was observed at 0.23 V in the reverse scan. The electrochemical reaction for the 40-bilayer LPEI–RuP nanocomposite film is completely reversible at low scan rates up to 50 mV s^{-1}, which shows that even thick films (>1 μm) are fully electrochemically accessible. At higher scan rates the film is partially reduced and the sharp peaks of oxidation and reduction broaden and become flat. The broadening of the peaks is attributed to the presence of inactive LPEI present in the nanocomposite film; this increases the internal resistance of the film and the Li^+ ion insertion from the electrolyte to the electrochemical sites is more difficult. As explained by Ellis *et al.*,[19] at low scan rates the shape of the cyclic voltammogram is controlled more by the thermodynamic than the kinetic factors. The overall reaction mechanism does not change for different electrolytes but as reported by Chen *et al.*,[20] the E° values of the RuP seem to be affected by the type of cation (H^+, Li^+, Na^+, K^+, Rb^+) in the electrolytic solutions. This could be due to the size of the cation, which plays an important role in the electrochemical behavior of the RuP films due to its inclusion and expulsion in the crystal lattice during potential cycling. According to the above discussion,

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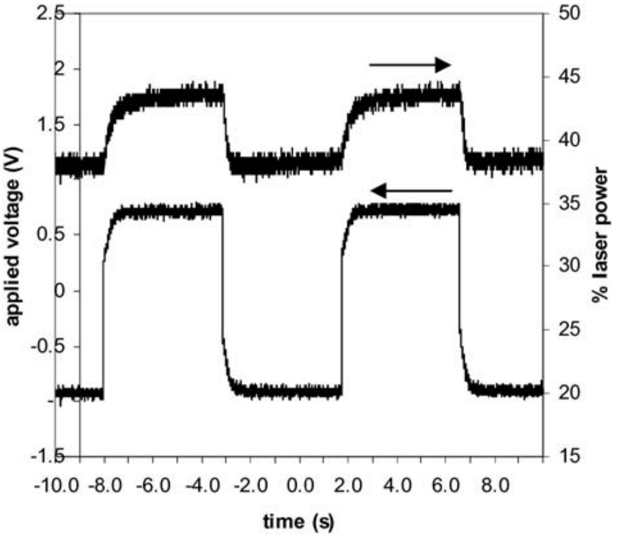

Fig. 4 Solid-state switching of a device (measured at 633 nm) consisting of a 40-bilayer LPEI–RuP film as a cathodically coloring material and a 40-bilayer PANI–PAMPS film as the anodically coloring material at -1 V to $+0.8$ V.

the redox reaction of the RuP in the case of Li^+ cations can be written as:

$$KFe^{III}[Ru^{II}(CN)_6] + Li^+ + e^- \leftrightarrow LiKFe^{II}[Ru^{II}(CN)_6] \quad (1)$$

The coloration efficiency was found to be 205 $cm^2\ C^{-1}$ for the present LPEI–RuP nanocomposites and is one of the highest reported for any inorganic electrochromic material. The charge per unit area required for the reduction process of RuP to RW is 4.16 mC cm^{-2} for a 40-bilayer film, which is the same number of bilayers used for CV, optical switching and UV–Vis absorption data. The Faradic charge associated with one bilayer for the process is 105 μC cm^{-2} and the surface coverage for each bilayer can be calculated by

$$\Gamma = Q/nF$$

where F is the Faraday constant (96.5×10^3 sA mol^{-1}). The surface coverage calculated using the above equation was found to be 1.1×10^{-9} mol cm^{-2}. This agrees well with the surface coverage expected for RuP nanoparticles of this size.[21]

Optical switching of RuP nanocomposite films was performed in both liquid electrolyte (see ESI Fig. S5†) and in solid-state devices. Solid-state devices were fabricated by depositing the LbL film on ITO coated glass in the same way as described in our previous work.[22] Two separate 40-bilayer films of PANI–poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) and LPEI–RuP were taken as complementary anodically and cathodically coloring materials, respectively. The $LiClO_4$–PC gel polyelectrolyte used for the solid-state device was synthesized as described by Sonmez *et al.*[23] The solid-state device switches from light blue to dark purple with coloration and decoloration times in the range of 600 ms and 300 ms, respectively, as shown in Fig. 4. The switching speed can potentially be improved by replacing LPEI with a cationic conducting polymer such as PANI, poly(phenylene vinylene) (PPV) *etc*. This is one of the first nanocomposite solid-state electrochromic devices reported in the literature.

In conclusion, RuP nanoparticles with spherical morphology were synthesized and thin film polymer–RuP nanocomposites were fabricated by the LbL technique. The absorbance of the film increases linearly with the number of bilayers deposited, indicating that thick nanocomposite films can be easily fabricated without sacrificing the individual contributions of the constituents. The 40-bilayer nanocomposite films show a very high contrast of around 84% with a high coloration efficiency of 205 $cm^2\ C^{-1}$. The change in color from purple–red (magenta) to transparent and switching in solid-state devices also fills in the gap in tri-color space of cyan, magenta, yellow (CMY) reflective displays described by DeLongchamp *et al.*[7] In this communication, our aim is to show the synthesis of RuP nanoparticles and the electrochromic properties of the polymer–RuP nanocomposites. Detailed electrochemical and multi-chromic studies and the effect of other polyelectrolytes will be presented in our forthcoming papers.

This material is based upon work supported in part by the U.S. Army Research Office under grant number W911NF-07-1-0452 Ionic Liquids in Electro-Active Devices (ILEAD) MURI.

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