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## A Simple Chemical Method for Deposition of Electrochromic Cobalt Hexacyanoferrate Thin Films

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### Abstract

In this work a simple chemical method for depositing cobalt hexacyanoferrate (CoHCF) films has been developed. The films have been prepared by successive immersion of the fluorine doped glass substrates (FTO) into an acidic aqueous solution of  $\text{CoCl}_2$  and  $\text{K}_4[\text{Fe}(\text{CN})_6]$ . The characterization of the films with X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Atomic force microscopy (AFM) showed that the films have crystalline structure. The electrochemical properties of the films were characterized by cyclic voltammetry. Obtained films exhibited electrochromism, changing colour reversibly between transparent and brown. Visible transmittance spectra of CoHCF films in their bleached and coloured states were recorded in-situ. Those spectra were used to estimate the optical band gaps. The dependence of the optical density on charge density was examined and used to calculate the colouration efficiency. The response times of the colouring and bleaching to an abrupt potential change from -2 V to +2 V and reverse were also examined. The maximum light intensity modulation ability of the films and saved energy, when the AM 1.5 spectrum is taken as an input, were calculated to be 55% and  $243.56 \text{ Wm}^{-2}$ , respectively, which makes this films suitable for application in electrochromic devices.

**Keywords:** Chemical deposition; Electrochromism; Cobalt Hexacyanoferrate; Thin films.

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## 1. Introduction

The ability of some materials to change reversibly their colour effected by the redox reactions, is known as electrochromism. Generally, electrochromic materials displayed distinct visible reversible colour changes between a transparent (bleached) and a coloured states, or between two coloured states, but there are also materials that exhibit several colours and are termed polyelectrochromic [1,2].

Over the past decade, a large number of scientific papers and patents have been issued in the field of electrochromism due to the increased research activity of the many scientists worldwide.

To date, a variety of applications of electrochromic materials such as smart windows for buildings and vehicles [3-6], sunglasses [7], antiglare mirrors [8], displays [9] and camouflages [10] have been widely researched. Especially, smart window represents a promising energy saving electrochromic device in green building to reduce the power consumption for lighting and air conditioning [11-13].

The research field of electrochromic compounds is very broad and includes the both organic and inorganic materials. Viologens, conducting polymers, metallopolymers and phthalocyanines are common organic electrochromic materials [14], while transition metal oxides and metal hexacyanometallates are common inorganic electrochromic materials [15].

In recent years, transition metal hexacyanoferrates, have raised renewed and growing interest not only because of their electrochromic properties [16-18], but also because of the peculiar properties such as electrocatalysis [19-21], ion exchange properties [22, 23], charge storage capabilities [24-26], and magnetic properties [27,28].

Transition metal hexacyanoferrate refers to Prussian blue (PB) [29, 30] and its analogs (PBAs) [18, 22]. They belong to mix-valence compounds which could be expressed with the generic formula,  $A_xM_k[Fe(CN)_6]_y \cdot mH_2O$ , where M is transition metal, A is alkali metal counter-cation necessary to ensure the electro neutrality, x, k, and y are stoichiometric coefficients, and m indicates the number of water molecules intercalated in the structure [31].

Among the PBAs, cobalt hexacyanoferrate (CoHCF) is considered as an attractive material because of the interesting physicochemical properties such as electrochromism, termochromism, photochemical magnetism, and electrocatalytic and sensing properties. CoHCF has general chemical formula  $A_xCo[Fe(CN)_6]_y$  except for the crystal water. As an electrochromic material, CoHCF has unique properties with colour changes dependent not only on its oxidation state, but also on the nature of counter cations incorporated in it during electro reduction [28]. On the other hand, the colour of the oxidized state of CoHCF depends on its chemical composition. It is known that CoHCF has two oxidized states with different spin configurations:  $A_xCo^{III}[Fe^{II}(CN)_6]_y$  (blue), and  $A_xCo^{II}[Fe^{III}(CN)_6]_y$  (red). With mixed oxidized state, CoHCF exhibits a brown-bleached colouration change [18].

CoHCF films were mostly prepared by different variations of electrochemical method [32-36], although chemical deposition was also reported [36]. The electrochromic properties of CoHCF thin films depend on their

structural, morphological and compositional characteristics, which, on the other hand, depend on the deposition method and deposition conditions [37].

The aim of this work is to investigate electrochromic properties of CoHCF thin films prepared by a new simple chemical deposition method, and their possible application in electrochromic devices for solar light modulation.

## **2. Experimental**

Prior the deposition, the substrates were degreased with hexane and then acetone. In the next step they were cleaned with detergent, alkaline solution, hydrochloric acid, and finally rinsed with deionized water and dried in air.

### **2.1. Preparation of the deposition solutions**

Two stock aqueous solutions of cobalt(II) chloride and potassium hexacyanoferrate(II) with volumes of 100 cm<sup>3</sup> were prepared. The 0.1 M cobalt(II) chloride solution was prepared by weighing out 2.379 g of cobalt(II) chloride hexahydrate, dissolving it in 100 mL volumetric flask in approximately 50 mL deionized water, and after dissolving, it was diluted up to desired volume of 100 mL. The 0.1 M stock solution of potassium hexacyanoferrate(II) with volume of 100 mL was prepared in a similar way by dissolving 4.224 g of potassium hexacyanoferrate(II) trihydrate in about 50 mL deionized water in 100 mL volumetric flask, and after dissolving, it was diluted up to 100 mL.

The chemical deposition of the cobalt(II) hexacyanoferrate thin films is carried out from two solutions. One of the solutions is prepared by mixing 30 mL 0.1 M aqueous solution of CoCl<sub>2</sub>, 60 mL H<sub>2</sub>O and 20 mL 3 M HCl in 150 mL laboratory beaker. The second solution is also aqueous solution prepared by mixing 30 mL 0.1 M K<sub>4</sub>[Fe(CN)<sub>6</sub>], 60 mL H<sub>2</sub>O and 20 mL 3 M HCl in 150 mL laboratory beaker.

### **2.2. The deposition of thin films**

The chemical deposition is carried out at room temperature by successive immersion of the substrate into two solutions. The experimental variables, such as pH, concentration, number of immersions, were optimized in pursuance of the best quality of the thin films. Prior to the deposition, 20 mL of each deposition solution was transferred to 25 mL laboratory beaker. Previously clean substrate was immersed into one solution and after 2 to 3 s in the other solution where it stays for the same time. These two immersions are count as one deposition cycle. The film thickness increases by increasing the number of deposition cycles. The final film thickness can be control and determined by counting the immersions of the substrate into one of the solutions. Throughout the deposition process the solution of CoCl<sub>2</sub> become pale pink, the K<sub>4</sub>[Fe(CN)<sub>6</sub>] solution become greenish, and the formed films are transparent. During the deposition after the tenth and then after each twentieth deposition cycle the substrate was rinse with water and gently rub down the thin film with a piece of cotton. This is necessary in order to provide cleaning of the surface by removing weakly sticking microcrystals and obtaining transparent films. At the end of the deposition the thin films were rinsed with water, rub down with cotton again, washed with deionized water and dried at ambient conditions. The as deposited thin films were transparent. The research

study was conducted with two kind of samples prepared with 100 and 200 deposition cycles and these corresponds on two thickness 370 and 690 nm respectively. The average increase in the growth in the film thickness in one deposition cycle was calculated to be about 3.6 nm. It can become higher if one uses higher concentrations of cobalt(II) chloride and potassium hexacyanoferrate(II) in their solution, but in that case the film will contain powder-like deposit.

### **2.3. Characterization of the thin films**

Commercially available fluorine doped tin oxide (FTO) - coated glass with dimensions of 50 x 20 mm and electric resistance of 10-20  $\Omega \cdot \text{cm}^{-2}$  were used as substrates. The XRD patterns of the thin films were recorded by Rigaku Ultima IV X-ray powder diffraction (XRPD) instrument.  $\text{CuK}\alpha$  radiation was used in the  $2\theta$  range of 5°-70°. The thickness and the surface morphology of the thin films was observed by Tescan, Vega 3LMU Scanning Electron Microscope. AFM micrographs were taken using Shimadzu Scanning Probe Microscope SPM-9700 in dynamic mode at room temperature. The chemical identification was conducted using Oxford X-act EDS. The samples for SEM and EDS analysis were gold coated by Quorum, Q150R ES Rotary Pumped Coating System.

The electrochemical measurements were carried out with cyclic voltammetry using a micro AUTOLAB II equipment (Eco-Chemie, Utrecht, Netherlands) in the potential range between -0.7 and -0.2 V. The electrochemical properties of the thin films were examined in 1M KCl aqueous electrolyte in conventional three electrode system consisting of CoHCF film/FTO as working electrode, Pt wire as counter electrode and KCl-saturated Ag/AgCl as reference electrode.

The optical spectra of the thin films, in their bleached and coloured states, were recorded in-situ by a Varian Cary 50 Scan spectrophotometer ranging from 350 to 900 nm. The working voltages in the range of  $\pm 2.0$  V were applied. The electrochromic, glass, home-made cell was used as a two electrode system. One electrode was a substrate with a thin film and the other electrode was a blank FTO substrate. The distance between the two electrodes in the cell was about 1 cm and 1M KCl aqueous solution was used as an electrolyte (~30 ml). The active surface area of the electrodes was about 8  $\text{cm}^2$ . An electrochromic cell with two clean FTO substrates filled with electrolyte was measured as 100 % background. Sequential potential switching measurements were carried out for response time ( $\tau$ ) calculations.

All reagents used during the experiments and the analysis were of analytical grade purity.

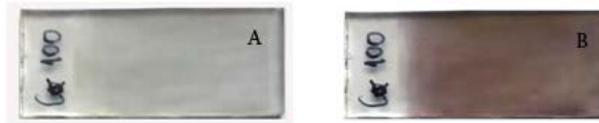
All as-deposited thin films with different thickness have passed an adhesiointape test.

## **3. Results and Discussion**

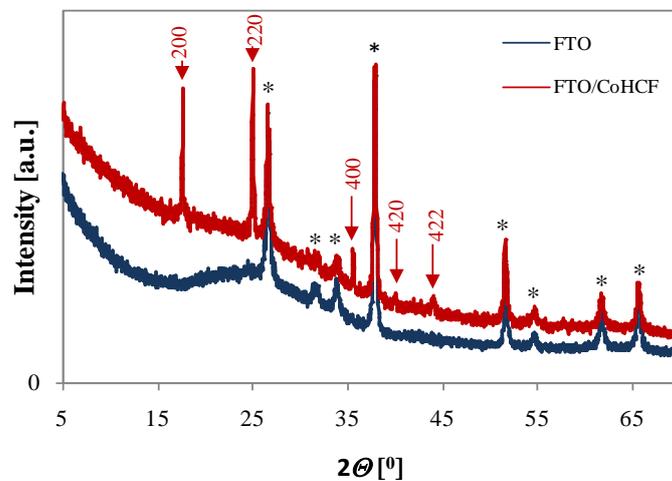
The CoHCF films prepared by chemical deposition method exhibited electrochromism. They were transparent in reduced state, and had a brown colour in oxidation state (Fig. 1).

Fig. 2 shows the diffraction patterns of the blank FTO substrate and CoHCF film deposited on FTO substrate. Diffraction peaks at: 17.62°, 25.02°, 35.58°, 40.06°, and 44.04°  $2\theta$  values belong to CoHCF (JCPDS No. 82–

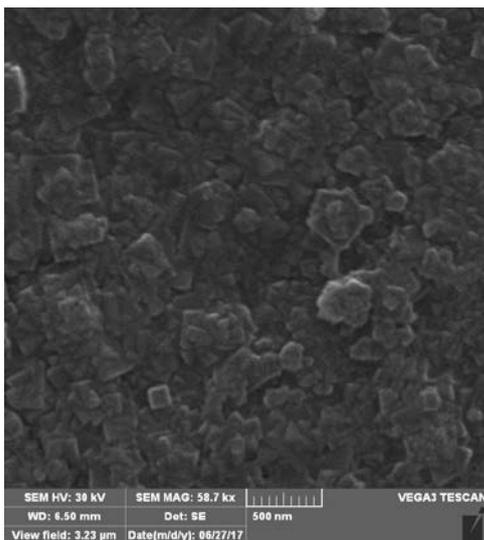
2284), and the other intensive peaks, denoted with asterix, belongs to FTO substrate. As can be seen, all the peaks related to CoHCF represent a typical face-centered cubic (fcc) structure [38]. From the diffractogram, the lattice constant was evaluated as 10.07 Å. This value of the lattice constant lies between the values of the Co(III)-Fe(II) state and the Co(II)-Fe(III) state, implying the mixed valence structure [18].



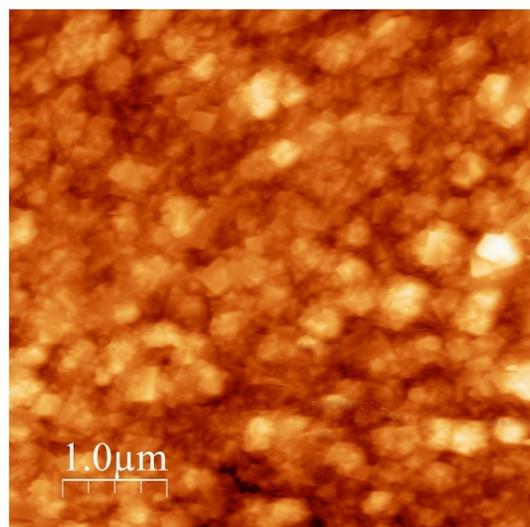
**Figure 1:** Photographs of chemically deposited CoHCF film in bleached and coloured states.



**Figure 2:** X-ray diffraction patterns of the blank FTO substrate and CoHCF film deposited on FTO substrate.



**Figure 3:** SEM microphotograph of the chemically deposited CoHCF film.



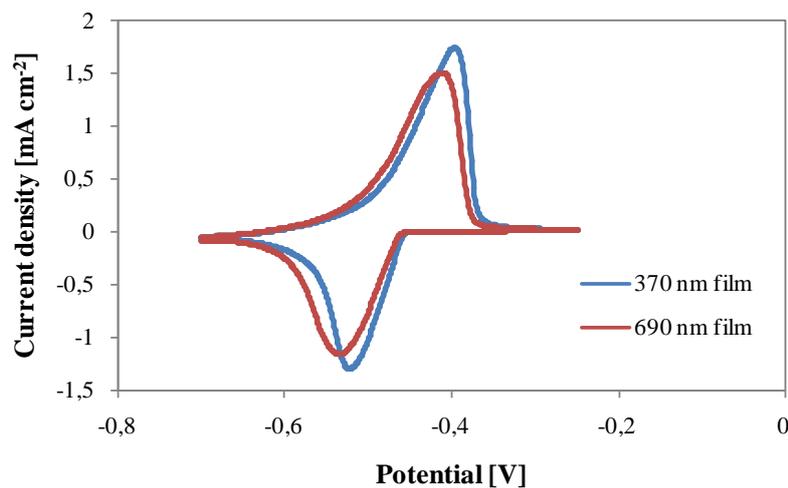
**Figure 4:** Two-dimensional AFM image of chemically deposited CoHCF film.

The surface morphology of CoHCF films was investigated using scanning electron microscope (SEM). The SEM microphotograph shown in Fig. 3 illustrates two dimensional image of film that has a rough surface and is formed of well-defined crystallites or crystal clusters with dimensions between 50 – 350 nm. The same results were obtained from the AFM microphotograph (Fig. 4).

The electrochemical properties of the CoHCF films were characterized by cyclic voltammetry (CV) measurements. Fig. 5 presents cyclic voltammograms of the CoHCF films with two different thicknesses (370 and 690 nm). The cycling was carried in 1M KCl aqueous solution in a potential range from -0.7 V to -0.2 V and back to -0.7 V. The potential scan rate was a 10 mV/s, and the films working area was 1 cm<sup>2</sup>. As shown in Fig 5, both films showed a clear redox reaction, indicating switching between reduced Co(II)-Fe(II) (transparent) state and Co(III)-Fe(II)/Co(II)-Fe(III) (coloured) state [18]. The diffusion coefficients through the anodic and cathodic cycles were estimated by the Randles-Sevcik equation [42]:

$$i_p = 2.72 \cdot 10^5 \cdot n^{3/2} \cdot D^{1/2} \cdot C \cdot v^{1/2} \quad (1)$$

Where  $i_p$  is the peak current density in A cm<sup>-2</sup> from cyclic voltammogram,  $n$  is the number of electrons transferred in the redox event, which is assumed to be unity,  $D$  is diffusion coefficient in cm<sup>2</sup> s<sup>-1</sup>,  $C$  is the electrolyte concentration in mol cm<sup>-3</sup>, and  $v$  is potential scan rate in mVs<sup>-1</sup>. The values of the electrochemical parameters determined from the CV curves (anodic,  $i_{pa}$  and cathodic,  $i_{pc}$  peak current density as well as the diffusion coefficient) are presented in Table 1. The diffusion coefficients are higher for the oxidation (colouring) than reduction (bleaching) process, which means that the deintercalation of the K<sup>+</sup> ions from the films goes faster than intercalation.

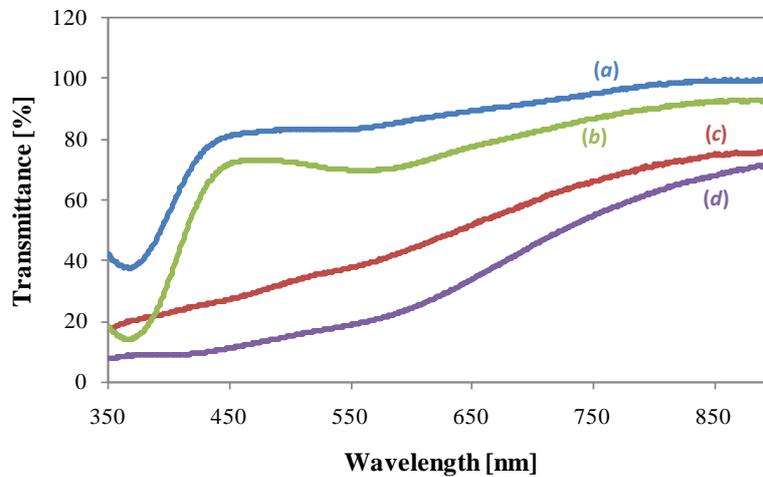


**Figure 5:** Cyclic voltammograms for 370 nm and 690 nm thick CoHCF films.

**Table 1:** Electrochemical parameters for chemically deposited CoHCF films.

Film thickness (nm)	$i_{pa}$ (mA cm <sup>-2</sup> )	$i_{pc}$ (mA cm <sup>-2</sup> )	Diffusion coefficient	
			$D_a$ (10 <sup>-9</sup> cm <sup>2</sup> s <sup>-1</sup> )	$D_c$ (10 <sup>-9</sup> cm <sup>2</sup> s <sup>-1</sup> )
370	1.73	-1.30	4.07717	2.30226
690	1.51	-1.16	3.10614	1.83309

The optical transmission spectra of the CoHCF films in the wavelength range from 350 to 900 nm in both, bleached and coloured states, taken *in-situ*, are presented in Fig. 6. As can be seen, maximum transmittance difference (about 50% for 370 nm thick films and 60% for the 690 nm thick films) occurs at around 450 nm.



**Figure 6:** Visible transmittance spectra of chemically deposited CoHCF thin films: (a) and (c) for 370 nm film – bleached and coloured states respectively; (b) and (d) for 690 nm film – bleached and coloured states respectively.

The visible transmittance spectra were used for calculation of the optical band gaps  $E_g$  of the CoHCF film. For that purpose, the absorption coefficient ( $\alpha$ ) was estimated from the transmittance data ( $T$ ) and the film thickness ( $t$ ) [39, 40]:

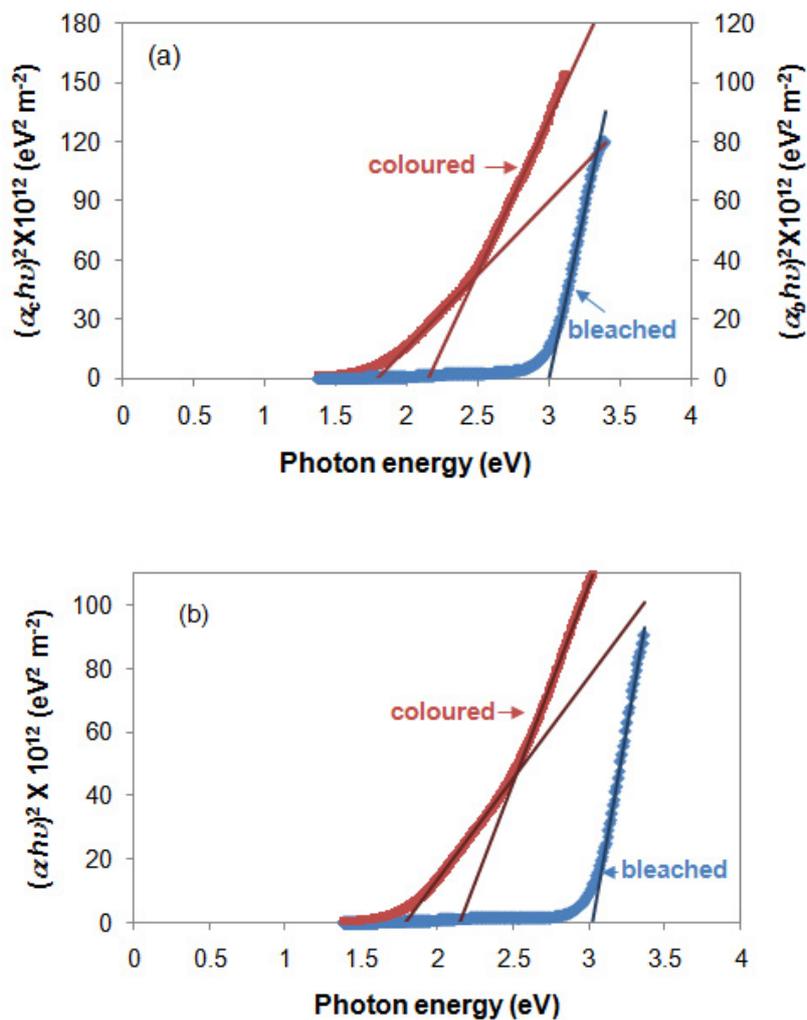
$$\alpha = \frac{1}{t} \ln \frac{1}{T} \quad (2)$$

The optical band gaps of the film were calculated from the absorption coefficient by fitting the data to the relation:

$$\alpha h\nu = B(h\nu - E_g)^m \quad (3)$$

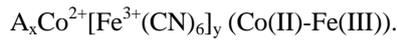
Where  $B$  is a constant,  $h\nu$  is the energy of the incident photon,  $E_g$  is the optical energy gap, and  $m$  is a number which determines the type of electron transition causing the absorption. The value of  $m$  is  $1/2$  for direct allowed,  $3/2$  for direct forbidden, 2 for indirect allowed, and 3 for indirect forbidden transitions.

The plots of  $(\alpha h\nu)^2$  versus  $h\nu$  for the chemically deposited CoHCF films in both, the coloured and bleached states, are presented in Fig. 7a (for the 370 nm thick film) and Fig. 7b (for the 690 nm thick film). The films showed direct electron transition mechanism in both states (bleached and coloured) of the film. The optical energy gaps were calculated from the linear parts in the Fig. 7, as intercepts with the photon energy axes.



**Figure 7:** The plots of  $(\alpha h\nu)^2$  versus photon energy for chemically deposited CoHCF films: (a) 370 nm, and (b) 690 nm thick film.

The obtained results for the optical energy gaps of the films in their bleached and coloured states are presented in Table 2. The presence of two band gaps in the coloured (oxidized) state of the films could be ascribed to coexisting of both oxidized states with different spin configurations:  $A_xCo^{3+}[Fe^{2+}(CN)_6]_y$  (Co(III)-Fe(II)) and



**Table 2:** The optical band gaps estimated from Figure 7

Film thickness (nm)	$E_g$ (bleached) (eV)	$R^2$	$E_g$ (coloured) (eV)	$R^2$
370	3.001	0.998	2.148	0.998
690	3.019	0.997	2.145	0.99750

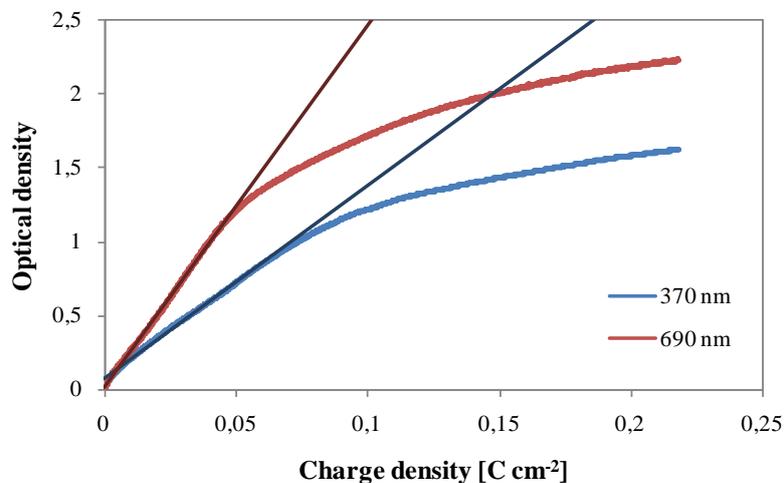
An important parameter for the characterization of electrochromic films is the colouration efficiency, which determines the amount of optical density change ( $\Delta OD$ ) induced as a function of the injected/ejected charge ( $\Delta Q$ ). It is given by the equations [41]:

$$\eta = A \frac{(\Delta OD)}{\Delta Q} \tag{4}$$

and

$$(\Delta OD) = \ln \frac{T_b}{T_c} \tag{5}$$

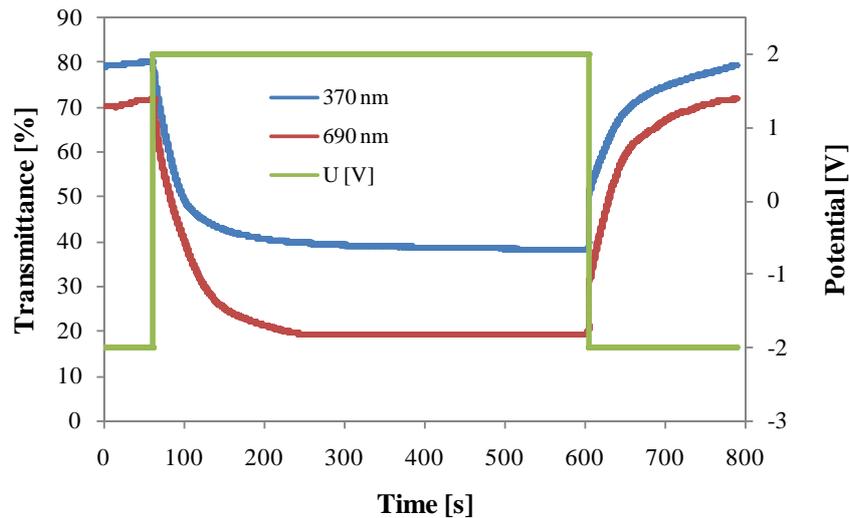
Where  $\eta$  is the colouration efficiency at given  $\Delta Q$ ,  $T_b$  and  $T_c$  are the bleached and coloured transmittance values, respectively,  $\Delta Q$  is the injected/ejected charge during the colouration process, and  $A$  is the active area of the electrochromic film. In this work, the colouration efficiency was calculated from  $(\Delta OD)$  at 550 nm and  $(\Delta Q/A)$ , during the colouration, after the film was fully bleached.



**Figure 8:** The dependence of the optical density on the charge density at 550 nm for 370 and 690 nm thick film.

Electrochromic colouration efficiency ( $\eta$ ) was determined from the plot of the optical density change against the charge per unit area ( $Q/A$ ), displayed in Fig. 8. The colouration efficiency at 550 nm was extracted as the slope from the line fitted to the linear part of the curve. The calculated  $\eta$  values were found to be  $24.6 \text{ cm}^2 \text{ C}^{-1}$  and  $13.1 \text{ cm}^2 \text{ C}^{-1}$  for the 370 nm and 690 nm films respectively. Similar values were referred in [42].

In order to determine the response time, the time dependence of transmittance due to the abrupt potential switching between  $\pm 2\text{V}$  was recorded in-situ and presented in Fig. 9.

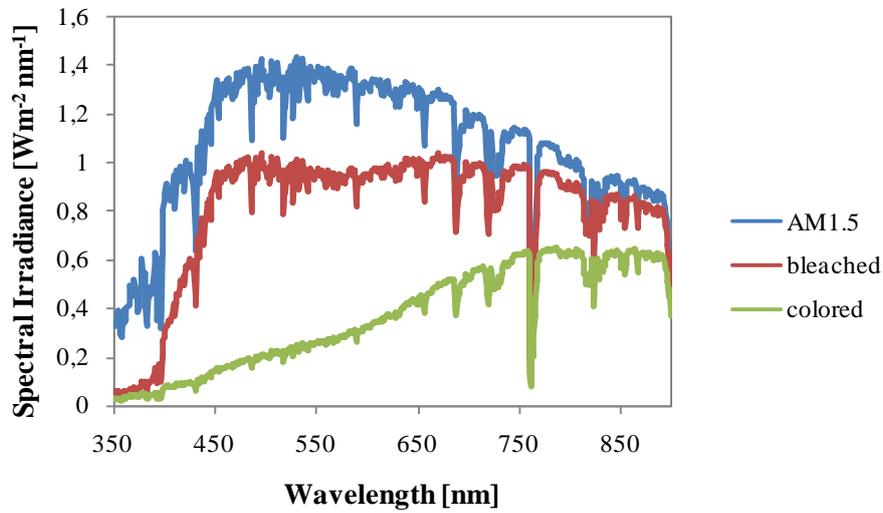


**Figure 9:** The time response of the transmittance at 550 nm of the 370 nm and 690 nm thick CoHCF films.

The response time  $\tau$  was determined as the time needed for the film to reach 80% of the final change in the transmittance. According to this criterion, the response time was found to be 50 s for colouring, and 57 s for bleaching (370 nm thick film), and 64 s for colouring and 57 s for bleaching (690 nm thick film). As can be seen, the colouration time of the chemically deposited CoHCF films, increases with the increasing of the film thickness, while the bleaching time remains the same. Finally, the output integral of the spectral intensity, the integral of the spectral modulation, and the saved energy were calculated using the solar irradiance spectrum AM1.5 for a normal incident illumination on a CoHCF based electrochromic device (glass/FTO/CoHCF/electrolyte/FTO/glass) and the transmittance spectra of the CoHCF film in the bleached and coloured states [43]. The irradiance of the solar spectrum AM 1.5 [44] and the transmittance spectra of the chemically deposited CoHCF films in their bleached and coloured states were taken as input parameters. The output spectral intensities transmitted across the CoHCF films were calculated and presented in Fig 10. The integrated intensity modulation was estimated with the following equation:

$$\text{Modulation} = \frac{\int_{\lambda_m}^{\lambda_n} (T_b(\lambda) - T_c(\lambda)) \cdot I(\lambda) d\lambda}{\int_{\lambda_m}^{\lambda_n} T_b(\lambda) \cdot I(\lambda) d\lambda} \quad (6)$$

Where  $T_b$  and  $T_c$  are transmittance at the bleached and the coloured states, respectively,  $I(\lambda)$  is solar irradiation intensity at a specific wavelength ( $\text{W m}^{-2} \text{nm}^{-1}$ ).



**Figure 10:** Spectral intensity of the transmitted AM 1.5 solar irradiance spectrum through the CoHCF film in the bleached and coloured states

The solar energy is calculated by integrating the solar intensity within the wavelength ranging from 350 nm to 900 nm, and the difference between the integrated intensities in the bleached and the coloured state is deemed as saved energy [45]. The results of the numerical integration for the spectral intensity within the visible region (350-900 nm), together with the solar energy modulation and saved energy, are presented in Table 3.

**Table 3:** Integral transmitted intensity ( $I_t$ ) from 350 to 900 nm through the CoHCF film in its bleached and coloured states, together with the solar energy modulation and saved energy.

State	$I_t$ ( $\text{W m}^{-2}$ )	Modulation (%)	Saved energy [ $\text{W m}^{-2}$ ]
bleached	443.60	55	243.5650
coloured	200.04		

As can be seen in the Table 3, the estimated integrated intensity modulation and saved energy are 55% and  $243.56 \text{ Wm}^{-2}$ , respectively. These considerable values give the opportunity for implementation of the chemically deposited CoHCF films in electrochromic devices for solar light modulation.

#### 4. Conclusions

CoHCF films were successfully prepared onto FTO coated glass substrates by chemical deposition method. The described method is economical, not requires sophisticated equipment, and offers a possibility for large area depositions. The chemicals are available and relatively cheap. X-ray, SEM-EDS and AFM analysis show that the films have a rough surface and are formed of well defined crystallites or crystal clusters with dimensions

between 50-350 nm. The obtained films exhibited good electrochromic properties. They were stable and exhibited good reversibility, with colour changed from originally transparent to brown colour when positive potential was applied, and back to transparent when potential was reversed. The optical and electrochromic properties of the films are convenient for visible light intensity modulation applications. The maximum difference in the transmittance between the transparent and coloured states was found to be more than 50% at 450 nm. Optical energy gaps were estimated from the transmittance measurements for the both, transparent and coloured states of the films, assuming direct semiconductor transition mechanism. The colouration efficiency was found to be less than  $25 \text{ cm}^2 \text{ C}^{-1}$  with tendency to decrease with the film thickness. The switching times between transparent and brown states were found to be 50 s (370 nm film) and 64 s (690 nm film) for colouring, and 57 s for bleaching, for the both films. The maximum light intensity modulation ability of the films and saved energy were calculated to be 55% and  $243.56 \text{ Wm}^{-2}$ , respectively, which makes chemically deposited CoHCF suitable for application in electrochromic devices.

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