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High contrast and low-driving voltage electrochromic device containing triphenylamine dendritic polymer and zinc hexacyanoferrate



Sheng-Yuan Kao^a, You-Shiang Lin^b, Kevin Chin^a, Chih-Wei Hu^a, Man-kit Leung^{b,c,*}, Kuo-Chuan Ho^{a,c,**}

^a Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

^b Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan

^c Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

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ABSTRACT

A new electrochromic device (ECD), in which poly(N',N'',N'''-tris[N,N-bis-(4'-diphenylamino-biphenyl-4-yl)phenyl]-1,3,5-benzene-tricarboxamide) (PG1) acted as the electrochromic film and zinc hexacyanoferrate (ZnHCF) as an ion storage material, was proposed. ZnHCF was observed to exhibit high charge capacity while maintaining high transparency when undergoing redox reaction. This ECD shows two-stage electrochromism and both transitions exhibit significant transmittance change (> 60% at 490 and 740 nm). Low-driving voltage (from -0.4 to 0.1 V) was also observed when switching in the first transition. This ECD also exhibits a very stable behavior (no significant decay for the transmittance change at 490 nm after 4000 cycles) when operating in the first transition.

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1. Introduction

Electrochromism is a science that studies reversible color switching in materials when applying a dc voltage [1,2]. The modulated electronic device that incorporates this technology is called electrochromic device (ECD). Up to date, this technology is mostly researched for the commercial product of energy-saving smart windows [3–7]. Other applications, such as anti-glare rearview mirrors [8], safety helmets [9] and display devices [10], have also been reported.

Conducting polymers [10–17], which usually exhibit high color contrast and offer multiple colors, recently gained their popularity. It is generally accepted that triphenylamine (TPA) based polymers exhibit promising electrochromic behaviors, including significant transmittance change and multi-stages electrochromism [18–22]. On the other hand, dendritic monomers possess high solubility

and low viscosity, allowing them for easy electrodeposition [21]. Besides, polymer with alternating electron poor and rich group was reported to show better cycling stability [2]. These qualify poly(N', N'', N'''-tris[N,N-bis-(4'-diphenylamino-biphenyl-4-yl)phenyl]-1,3,5-benzenetricarboxamide) (PG1) [21] a good candidate for electrochromic material in this study.

PG1 can be obtained simply by electro-polymerization. The applied positive potential would expel an electron on nitrogen atom in G1 monomer and form a radical at the tip of its TPA group through resonance. A covalent bond was formed when two radicals meet and polymerize to PG1, thus forming a structure named tetraphenylbenzidine (TPB) [23]. TPB gives two-stage electrochromism [19], from which PG1 exhibited its electrochromic properties.

A modulated ECD has been found to perform best when the charge capacities of both films are matched [24]. Ion storage material can provide sufficient charge capacity while not sacrificing the transparency of an ECD [25–28]. Inorganic materials are preferred ion storage materials since they possess larger charge capacity comparing to conducting polymers. A Prussian blue analog, zinc hexacyanoferrate (ZnHCF), was reported to satisfy these requirements [29]. Nevertheless, it has been suffering from lack of uniformity in film preparation, thus only few reports have

* Corresponding author at: Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan. Tel.: +886 2 3366 1673; fax: +886 2 2363 6359.

** Corresponding author at: Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan. Tel.: +886 2 2366 0739; fax: +886 2 2362 3040.

E-mail addresses: mkleung@ntu.edu.tw (M.-k. Leung), kcho@ntu.edu.tw (K.-C. Ho).

utilized this material for electrochromic applications. Recently, Gotoh et al. have proposed a process for synthesizing water-dispersible particles of Prussian blue and its analogs [30], including ZnHCF [31]. Thereafter, Hong et al. [32,33] has published papers using mixture of ZnHCF and poly (styrenesulfonate) doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) as ion storage material in ECDs. Aside from previous reports, we have fabricated the ZnHCF ion storage material that exhibiting desired performance without the assistance of PEDOT:PSS.

In this work, we fabricated an ECD consisted of an electrochromic conducting polymer named PG1 (the structure is reported in [21] and depicted in Fig. S1 in the electronic supplementary information, ESI) and an ion storage material ZnHCF. PG1 possesses two-stage electrochromism with high color contrast [21], thus eliminating the need of a cathodically coloring film as the counter electrode. In this study, ion storage material, ZnHCF, was chosen as the counter electrode. The proposed ECD exhibits sufficient transmittance change ($> 60\%$ at 490 nm) with high reversibility. In particular, this ECD requires only a very small potential window (0.5 V), making it a promising candidate not only for ECD alone, but for incorporating into a photoelectrochromic device (PECD).

2. Experimental

2.1. Materials

LiClO_4 (95%), tetrabutylammonium perchlorate (TBAP, $> 99\%$) and propylene carbonate (PC, 99%) were purchased from Alfa Aesar. Ortho-dichlorobenzene (ODCB, 99.7%) was purchased from TEDIA. ZnCl_2 ($> 98\%$) and $\text{Na}_4\text{Fe}(\text{CN})_6$ ($> 99\%$) were purchased from Aldrich. The G1 monomer ($> 99\%$) was synthesized as suggested in previous work [21], which is briefly shown as Scheme S1 and Scheme S2 in the ESI. Before use, PC was dehydrated using 4-Å molecular sieve from Acros while other chemicals were used as received without further purification.

Indium tin oxide (ITO, Solaronix SA, $R_{\text{sh}}=7 \Omega/\square$) glass was used as the conducting substrate for coating electrochromic or ion storage thin films. The ITO glass was cleaned by isopropyl alcohol and treated by ozone for 20 min before film deposition. Characterization of a thin film was done in a three-electrode system, where a thin film-coated ITO electrode was assigned as the working electrode, homemade Ag/Ag^+ electrode as the reference, and $1 \text{ cm} \times 4 \text{ cm}$ platinum foil as the counter electrode.

2.2. Preparation of PG1 and ZnHCF thin films

PG1 thin film was electro-deposited in a three-electrode system by applying a potential step of 1.3 V in a precursor solution, which contained 1.0 mM G1 monomer and 0.1 M TBAP in ODCB. The deposited charge capacity of PG1 was controlled to be $10.0 \text{ mC}/\text{cm}^2$ to obtain the largest transmittance change. The PG1 modified ITO electrode was then stored at room temperature.

Water-dispersible ZnHCF was prepared according to the method proposed by Gotoh et al. [30] and Lee et al. [31]. Briefly, ZnCl_2 (0.5452 g) and $\text{Na}_4\text{Fe}(\text{CN})_6$ (0.9681 g) aqueous solutions were mixed and the resulting white ZnHCF precipitate was washed by deionized water (DIW) extensively. The washed precipitate was introduced into 50 ml aqueous solution which contained 0.23 g $\text{Na}_4\text{Fe}(\text{CN})_6$ that acted as ligands to modify the surface of ZnHCF precipitation. This aqueous mixture was vigorously stirred for at least 72 h. The whitish water-dispersible ZnHCF powder was obtained after removing water.

The water-dispersible ZnHCF ink was obtained by introducing 0.1 g of water-dispersible ZnHCF powder into 1 ml DIW. ZnHCF

film was prepared by spin coating after water-dispersible ZnHCF ink was dropped onto the ITO. The spin coating conditions were controlled to be 1500 rpm for 10 s. The ZnHCF film was stored at room temperature before characterization.

2.3. Assembly and characterization of ECD

The electrolyte used for this study is 0.1 M LiClO_4/PC . Before assembling, both PG1 and ZnHCF films were pretreated by cyclic voltammetry (CV) in a three-electrode system between 0.2 and 0.8 V for 20 cycles. Then PG1 modified electrodes were bleached for 30 s at 0 V.

The ECD was assembled by laminating the bleached PG1 film and ZnHCF film. The electrolyte, 0.1 M LiClO_4/PC , was sealed in between the two electrodes separated by a 3 M spacer tape (cell gap was ca. 0.14 mm). In the subsequent characterization, PG1 coated ITO electrode was assigned as the working electrode.

2.4. Measurements

Electrochemical characterization was done by using a potentiostat/galvanostat (Autolab, model PGSTAT 30). Spectrophotometer (Ocean Optics, DH-2000-BAL) was used in conjunction with the potentiostat/galvanostat to conduct in-situ UV-vis measurement. Baseline of in-situ UV-vis measurement was carried out on a blank cell containing working electrolyte before obtaining the spectra of thin films, while the baseline was done on air when measuring spectra of ECDs. The ZnHCF powder was characterized by X-ray diffraction (XRD) patterns (Rigaku, Ultima IV) with $\text{Cu K}\alpha$ radiation to verify its composition. The morphology of ZnHCF was observed by scanning electron microscope (SEM, NOVA™, Nano SEM 230). Particle size of ZnHCF was also verified by dynamic light scattering (DLS, Brookhaven Instruments Corporation, 90Plus/BI-MAS).

3. Results and discussion

3.1. Characterization of ZnHCF and PG1 thin films

The water-dispersible ZnHCF powder was subjected to X-ray diffraction and the result is shown in Fig. 1. All peaks in the XRD pattern can be assigned to $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ (JCPDS, PDF no. 38-0688), suggesting the complete removal of the excess reagent during washing.

The DLS data for the powder dispersed in DIW are shown in Fig. S2. The z-average value was reported to be 179.7 nm with a standard

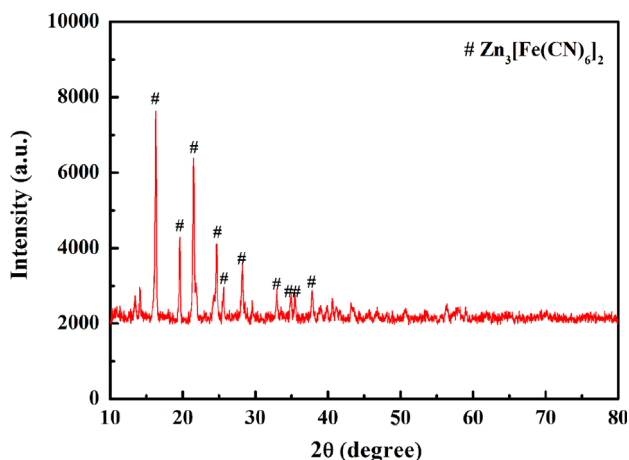


Fig. 1. XRD pattern of water-dispersible ZnHCF powder.

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