Supplementary Information

Electroactive Subwavelength Gratings (ESWGs) from Conjugated Polymers for Color and Intensity Modulation

Thiruvelu Bhuvana, Byeonggwan Kim, Xu Yang, Haijin Shin and Eunkyoung Kim*

Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Republic of Korea

*E-mail: eunkim@yonsei.kr

Section 1.Theory for Subwavelength Diffraction

In general, a line grating structure consists of many slits of width w and grating period d. When a monochromatic light with a wavelength λ passes through such grating structures, a diffraction pattern is generated following the diffraction equation, $m\lambda = d(\sin\alpha + \sin\beta)$where λ is the wavelength of the incident light; d is the grating period; m is the diffraction order; α is the incident light angle, and β is the diffracted light angle. The position of the maxima is given by the angle β. The central maxima when $m = 0$ is the zeroth order diffraction, while the successive maxima on either side are the mth order diffraction ($m = 1, 2, 3$, etc). For $d<\lambda$, the diffraction is suppressed as the diffraction angle becomes imaginary for all orders m except for the zeroth order diffraction. This condition holds good for SWGs. Conceptually, the light propagating through a SWG structure'senses' the average optical properties of the SWG medium. Hence, it can be represented as a locally homogeneous and uniaxial birefringence medium.[1]The effective refractive index of this new medium is defined as[1]

$$n_{eff} = \sqrt{n_0 n_1} \qquad \text{(S1)}$$

where$n_0$and n_1 are the refractive index of the surrounding medium and the grating material, respectively. The light that is reflected or transmitted through these SWGs follows Snell's law. The refractive index of the electrolyte solutions (n_1) $LiClO_4$/ACN and LiBTI/PC was determined as 1.345 and 1.418, respectively by Abbe's refractometer.

When SWGs are illuminated with a white light source, which consisted of all wavelengths in the visible spectral range, different colors are generated based on the angle of incidence both in the transmission and reflection mode. In the refection mode, they simply work as colored mirrors.[2]The color of the zeroth order reflected light depends on the angle of incidence and the grating parameters such as d and the thickness, t, of the grating, the refractive indices of the grating material, and the surrounding medium. For a given grating, depending on the angle of incidence, different colors are reflected for the thickness $t \geq \lambda/4n_{eff}$ and $n_{eff}>n_{surr}$ (the refractive index of the medium interfacing with the SWG). These are important conditions, which ensure that constructive and destructive interferences occur for some wavelengths of white light to obtain an individual color at the zeroth order diffraction.

For a square wave phase grating, the diffraction efficiency, *DE* of the zeroth order can be calculated based on the following equations[3]:

$$DE_{m=0} = cos^2(\xi/2) \tag{S2}$$

where ξ is the phase difference between the grating material and the surrounding medium; the line grating creates a spatially periodic modulation of the refractive index, and the ξ depends on the peak-to-peak amplitude path of the light expressed as[3]

$$\xi = 2\pi t\, (n_0 - n_1)/\lambda \tag{S3}$$

Where n_0 and n_1 are the refractive index of the grating material and surrounding medium, respectively. From equations S2 and S3, it is evident that the *DE* is a function of ξ,and in principle, the intensity of the zeroth order can be modulated from the maximum (100%) to 0% by varying ξ. For a given λ, any variation in t or Δn will influence ξ, which in turn can be used to modulate the intensity of the reflected and transmitted light. In the present study, at a fixed angle of incidence and for a given thickness of the grating, a change in Δn results in a change in the diffracted intensity. Since the refractive index of the electroactive polymer can be reversibly changed by electrochemical (EC) doping and dedoping of a polymer for a given thickness, the intensity of the color from the ESWGs can be conveniently modulated by an

ECdevice consisting of a polymer grating and an electrolyte. Therefore for a given grating, firstly, full spectral colors are obtained by varying the angle of incidence and secondly, at fixed angle of incidence, for specific color, the color intensity can be varied by applied potential, without changing the thickness of the polymer gratings or surrounding medium. As the doping states are kept stable once they reached,[4] the color and its intensity are kept with a long memory even after the electric supply is turned off. The electric supply for this system is only used for the switching of color intensity and not necessary for displaying static images. Therefore, the ESWGs displays in this work provide low energy consumption displays.

Section 2.Experimental Details

The AFM profile of PDMSPattern.AFM profile of the PDMS stamp is provided in Figure S1 with its thickness profile. The relief features are 420 nm wide with their height being 120 nm. They are separated by 180 nm.

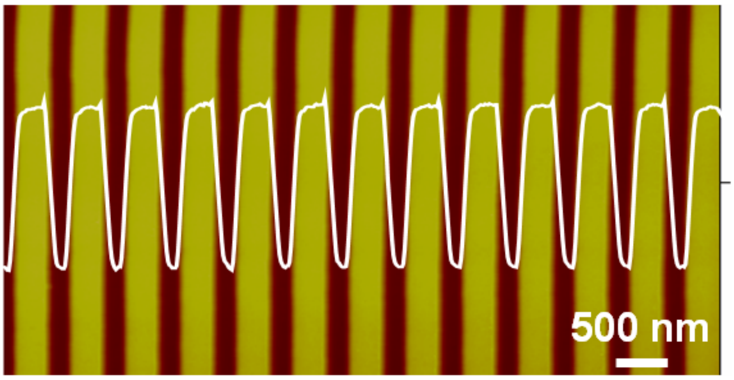

Figure S1. AFM image and its z-profile for PDMS stamp used for patterning.

Cyclic Voltammograms (CVs) of Polymers. The results of CV measurement carried out on the two polymers in 2-electrode set-up with the scan rate of 50 mV s^{-1} are shown in Figure S2.

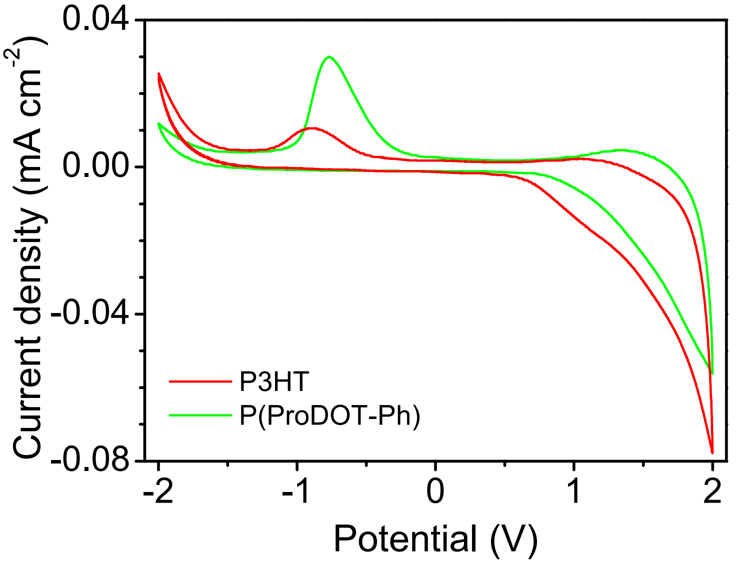

Figure S2. Cyclic voltammograms for patterned P3HT and P(ProDOT-Ph) films performed in a 2-electrode system.

On application of -2 V the polymers is in their neutral state, they remain so till the application of 0 V. The deviation in their behavior gets reflected in the voltage range higher than 1 V. At 1.1 V, P3HT begins to gets oxidized whereas for P(ProDOT-Ph) it begins around 1.4 V.

Cyclability of ESWGs: The cyclability of ESWGs of P(ProDOT-Ph) by change in the diffracted intensity in response to an alternative step potential between -2 and 2 V with a switching time of 10 seconds for 100 cycles is shown in Figure S3. The intensity is completely reversible in this potential range.

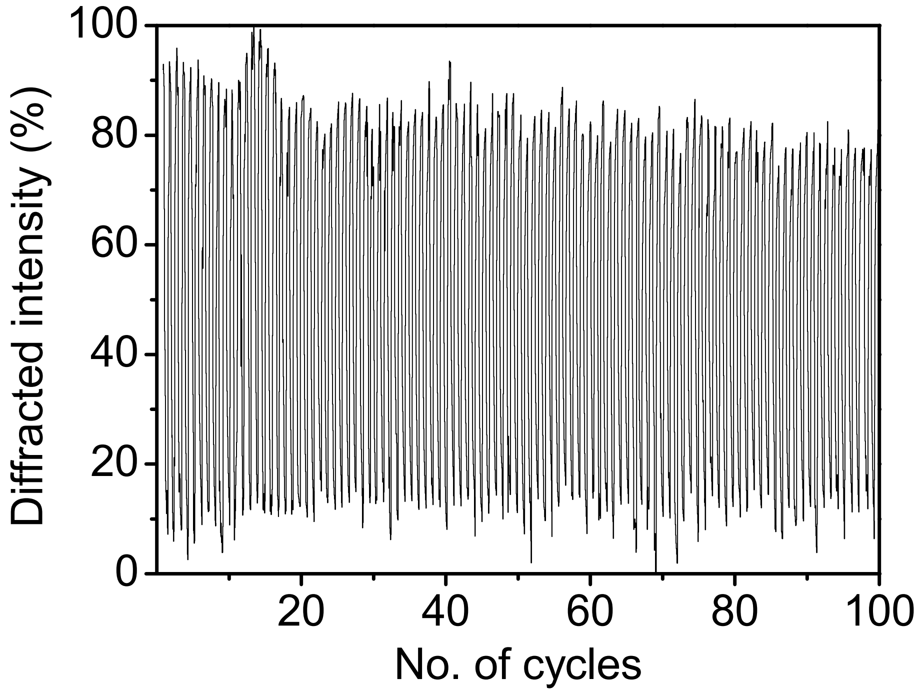

Figure S3. A plot of the variation in diffracted color intensity with external potential switched between -2 and 2 V every 10 seconds for the ESWGs of P(ProDOT-Ph).

Reference

1. H. Kikuta, H. Toyota and W. Yu, *Opt. Rev.,* 2003, **10**, 63.

2. K. H. Knop and R. H. Morf, US Patent No. 4484797, 1984.

3. Z. G. Li, Y. Yang, X. M. Zhang, A. Q. Liu, J. B. Zhang, L. Cheng and Z. H. Li, *Biomicrofluidics*, 2010, **4**, 043013.

4. J. Kim, J. You, B. Kim, T. Park and E. Kim, *Adv. Mater.,* 2011, **23**, 4168.