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# Development and application of patterned conducting polymer thin films as chemoresponsive and electrochemically responsive optical diffraction gratings

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Dedicated to Professor R. Parsons on the occasion of his retirement from the position of Editor in Chief of the Journal of Electroanalytical Chemistry and in recognition of many contributions to electrochemistry

## Abstract

We describe the preparation of two-dimensionally patterned polyaniline (PANI) thin films via microtransfer molding and electropolymerization techniques. This procedure yields reproducible conducting polymer patterns with excellent feature periodicity, making them useful as diffraction gratings. The fabricated polymer gratings were characterized via tapping-mode atomic force microscopy. Spectroelectrochemistry was used to characterize the optical properties associated with various intrinsic PANI redox states. In accordance with the Kramers–Kronig relation for change-in-absorptivity and change-in-index-of-refraction, electrochemically induced changes in refractive index (detected via changes in diffraction efficiency) were observed to coincide with electrochemically-induced changes in the PANI electronic absorption spectrum. In addition, the higher oxidation states of PANI and the associated changes in refractive index proved accessible via chemical oxidation. Beyond the novelty of a chemically-switchable transmission grating, the response of this system points to the possibility of developing diffraction-based chemical sensing schemes. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Optical diffraction gratings; Electrochemical sensors; Polyaniline

## 1. Introduction

Conducting polymers have attracted considerable attention as candidate materials for applications in catalysis [1–3], sensing [4–7], and microelectronics [8–10]. One of the most widely studied conducting polymers is polyaniline (PANI) which has proven useful in a variety of capacities ranging from biochemical sensing [11,12] to battery materials [13,14]. In this study, we report the fabrication of a chemically and electrochemically switchable polyaniline diffraction grating (2-D grating) produced by microtransfer molding and characterized by atomic force microscopy (AFM) and relative diffraction efficiency measurements. We suggest that the diffraction modulation phenomenon may prove useful in

the context of chemical sensing and present relevant background studies here.

The majority of chemical sensors employ voltammetric [15–17], conductivity [18–21], or absorptivity [22–25] changes as modes of detection; however, apart from surface-plasmon-resonance methodologies [26–28], relatively little attention has been focused on index of refraction changes. A chemical or electrochemical event that induces a change in light absorption or electrical conduction may also change the effective index of refraction of a material [29–32]. This change may be brought about by a change in the dielectric constant of the material itself or through displacement of interstitially packed entities in favor of higher or lower index molecules. If a sensing material is characterized by periodic modulation of the index of refraction in one, two, or three dimensions, changes in the index can be readily detected via diffraction efficiency measurements, where such measurements entail simply monitoring

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light intensities at different locations of constructive interference.

In the present study, electrochemically-induced changes in UV–vis spectra of PANI films were found to predict well the corresponding changes in diffraction efficiency of PANI gratings. In addition, higher oxidation states of the polymer were found to be accessible through chemical oxidation. Upon chemical oxidation, the PANI diffraction gratings exhibit dramatic changes in diffraction efficiency, suggesting that the change in diffraction efficiency response might be utilized for oxidant sensing.

## 2. Experimental

### 2.1. Substrate patterning and film deposition

The patterned polyaniline films used here were fabricated via successive microtransfer molding [33,34] and electropolymerization steps. Using a previously described method [35], polydimethylsiloxane (PDMS) stamps for microtransfer molding were fabricated by curing a 10:1 mixture of elastomer-hardener (Sylgard Silicone 184, Dow Corning) over a commercially obtained lithographic master (10  $\mu\text{m}$  pitch, AFM calibration grating, Digital Instruments) with etched square features approximately 185 nm deep, and laterally measuring  $5 \times 5 \mu\text{m}$  with a lattice constant of 10  $\mu\text{m}$ . The PDMS was cured at room temperature for 1 h, followed by additional curing at 60°C for 1 h.

Transparent, conductive indium-tin oxide (ITO) platforms (Delta Technologies, Ltd., 10  $\Omega/\text{square}$ ) were cleaned by immersion for 15 min in a heated (80°C) aqueous solution of ethanolamine (Aldrich, 20 wt%). The platforms were then rinsed several times in deionized water (MilliQ) and dried under a stream of nitrogen.

The PDMS stamp (overall dimensions of  $7 \times 7 \text{ mm}$ ) was inked with a 1:4 mixture of photoresist (Shipley Microposit 1827) and acetone, and quickly placed in contact with the conductive ITO surface. A light weight (approximately  $10 \text{ g cm}^{-2}$ ) was placed on top of the stamp to ensure conformal contact. The photoresist

was cured at 60°C for 15 min and the stamp was carefully peeled from the substrate.

Electrodeposition of PANI was performed using 0.2 M aniline (Aldrich) in 1.0 M HCl aqueous solution. Using a Bioanalytical Systems CV-27 potentiostat, the potential was cycled between  $-0.2$  and  $+0.85 \text{ V}$  versus  $\text{Ag}|\text{AgCl}|\text{KCl}_{\text{sat}}$  using the ITO platform as the working electrode and a Pt wire as the counter electrode. The potential was cycled for 15 min at  $50 \text{ mV s}^{-1}$ .

Following electrodeposition, the ITO electrode was quickly removed from the aniline solution and rinsed gently with distilled water. Photoresist liftoff was performed by soaking in acetone for 5 min. The electrode was then dried in a stream of nitrogen and stored under nitrogen until use.

### 2.2. Surface characterization

AFM was performed using a Digital Instruments Bioscope AFM head and a Nanoscope IIIa controller. All measurements were obtained in tapping mode with single etched silicon (TESP) Nanoprobe SPM tips (cantilever length 125  $\mu\text{m}$  and resonance frequency 307–367 Hz, Digital Instruments).

Non-patterned films for UV–vis absorbance measurements were prepared via electropolymerization and were subsequently electrochemically modulated using a Bioanalytical Systems CV-27 potentiostat. All electrochemical potentials were recorded relative to a  $\text{Ag}|\text{AgCl}$  reference electrode. All spectroelectrochemistry was performed in aqueous 0.1 M NaCl adjusted to pH 3 with HCl. All absorbance measurements were performed on a Hewlett–Packard 8452A diode array spectrophotometer.

### 2.3. Diffraction apparatus

Fig. 1 shows a schematic diagram of the apparatus used for diffraction efficiency measurements. Electrochemical diffraction modulation was performed in a quartz cuvette by using a Pine Instruments Model RDE4 potentiostat.

Chemical modulation of diffraction was accomplished by using a home-built diffusion cell that had been calibrated in concentration of  $\text{Br}_2$  gas as a function of time ( $\epsilon = 170 \pm 1 \text{ L mol}^{-1} \text{ cm}^{-1}$  at 416 nm) [36]. The cell displayed an initial lag time (no significant gas flow) of 4 min, followed by a roughly linear increase ( $3 \text{ ppm min}^{-1}$ ) in  $\text{Br}_2$  gas (Aldrich) concentration with time. PANI gratings and films were fabricated as detailed above and all UV–vis data were corrected for  $\text{Br}_2$  absorbance. All PANI films and gratings were used within 2 h of preparation.

The diffraction pattern produced by the fabricated polymer gratings is shown in Fig. 2. The light source

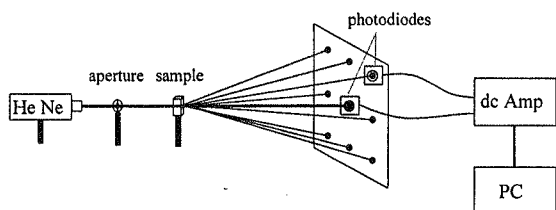


Fig. 1. Schematic diagram of the setup used to collect diffraction data and a digital photograph of a diffraction pattern produced by a 2-D PANI grating indicating the locations of constructive interference monitored during diffraction measurements ( $I_{0,0}$  and  $I_{1,1}$ ).

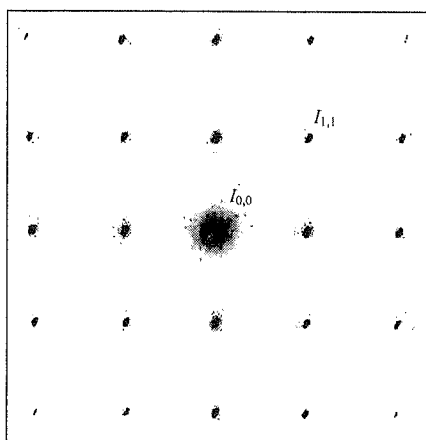


Fig. 2. Digital photograph of a diffraction pattern produced by a 2-D PANI diffraction grating used in this study.

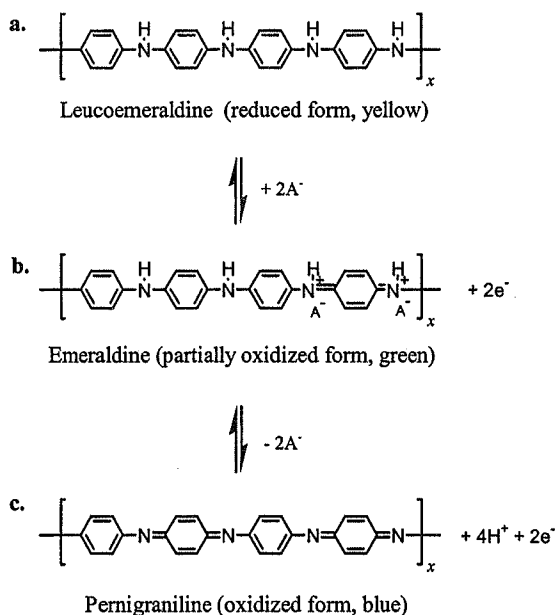


Fig. 3. Three predominant intrinsic redox states of polyaniline (PANI). (a) Leucoemeraldine, fully reduced ( $-0.2$  to  $+0.14$  V vs. Ag | AgCl); (b) emeraldine, partially oxidized ( $+0.14$  V to  $+0.45$  V vs. Ag | AgCl); (c) pernigraniline, fully oxidized ( $+0.45$  to  $1.00$  V vs. Ag | AgCl).

for diffraction efficiency measurements was a helium–neon laser (Uniphase 1508-0; 633 nm; 1 mW). The beam intensities,  $I_{0,0}$  (residual undiffracted light) and  $I_{1,1}$  ( $N = 1$ ,  $N' = 1$ ), were collected with silicon photodiodes (Thor Labs, 22.5V) which were aligned normal to the beams of interest. As seen in Fig. 1, a 2-D grating produces constructive interference spots in both  $x$  and  $y$  directions. Thus, the values for  $I_{1,0}$  and  $I_{0,1}$ , while equivalent to each other, are greater than for  $I_{1,1}$ . Analog signals were amplified with a custom-built dc amplifier and acquired via data acquisition software (Labview 3.1.1, National Instruments).

### 3. Results and discussion

#### 3.1. PANI redox behavior and grating structure

Polyaniline (PANI) can be synthesized in many different forms with multiple intrinsic redox states [37–39]. The generalized structure of PANI with three of the more prominent structures is shown in Fig. 3. The aniline polymers have the general formula  $[-B-NH-B-NH-]_y(-B-N=Q=N-)_{1-y}]_x$  in which B and Q denote the benzene rings in the benzoid and quinoid forms, respectively. Both the proton and anion are important factors in determining the redox state of the polymer and, indeed, the uptake or expulsion of either (or both) can result in changes in the oxidation state. An admittedly simplified, but useful, view is that the polymers are poly(*p*-phenyleneimineamine)s, in which the neutral intrinsic redox states can vary from the fully reduced leucoemeraldine (L,  $y = 1$ ), to the fully oxidized pernigraniline (P,  $y = 0$ ) form. The 50% oxidized polymer is referred to as emeraldine (E,  $y = 0.5$ ). Electrochemical or chemical oxidation of PANI can be modulated in a controlled manner either by applying a specific voltage, or introducing appropriate chemical agents (acids, bases, oxidants, reductants). The optical properties of PANI in these different oxidation states, as discussed further below, are nearly ideal for diffraction modulation studies at 633 nm.

An AFM image of a small portion of a typical PANI diffraction grating is shown in Fig. 4. The feature sizes are nearly uniform, and are approximately 300 nm in height. Local microstructure within each patterned square is characterized by spherical bundles ranging in size from approximately 30 to 200 nm, with a surface roughness of 64 nm (rms). Of particular interest is the clear periodicity of the patterned film which is essential for achieving the desired interference pattern. Pattern-

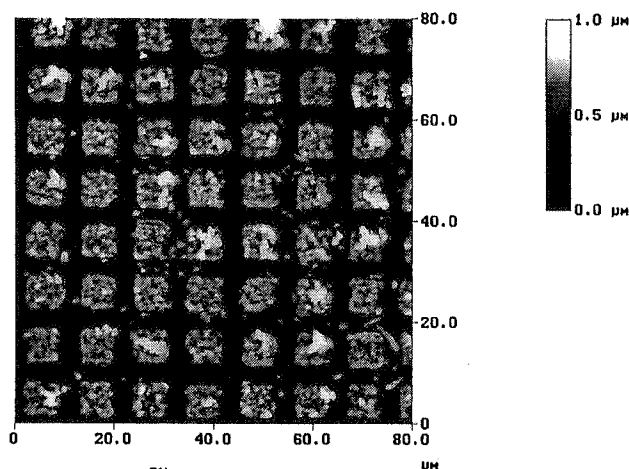


Fig. 4. AFM image of a patterned PANI diffraction grating showing periodicity and surface features.

ing of a dielectric material, such as a polymer or semiconductor, produces a spatially periodic modulation of the complex index of refraction (defined as:  $n' = n + ik$ , where  $n$  is the real index of refraction and  $k$ , the absorptivity, is the imaginary component) which, in turn, diffracts an incident beam of monochromatic light. In Fraunhofer type diffraction, constructive interference in each dimension occurs at:

$$N\lambda = d \sin \theta \quad (1)$$

where  $N$  is the order of diffraction ( $N = 1, 2, 3, \dots$ ),  $\lambda$  is the wavelength of incident light, and  $d$  is the periodic spacing of the pattern. Eq. (1) illustrates that the locations of in-phase interference are dictated by the lattice constant ( $d$ ) of the grating; however, the intensities at each point are determined by the periodic contrast of the refractive index (PCRI).

Directly related to the PCRI is the diffraction efficiency (DE) of a grating. In general, the DE of a grating can be defined as:

$$DE = \frac{\sum I_{\text{diff}}}{I_{\text{inc}}} \quad (2)$$

where  $I_{\text{diff}}$  is the intensity of a diffracted beam and  $I_{\text{inc}}$  is the incident intensity. Under resonance or near resonance conditions (and in the absence of scattering losses), the diffraction efficiency for a sinusoidal, one-dimensional (1-D) grating can be approximated by the following expressions [40,41]:

$$DE(\lambda) = \exp\left(\frac{-2.303OD(\lambda)}{\cos \theta}\right) \left[\frac{T}{\lambda \cos \theta}\right] [\Delta k(\lambda)^2 + \Delta n(\lambda)^2] \quad (3)$$

In the equation,  $\Delta k$  and  $\Delta n$  correspond to the difference in absorptivity and index of refraction between the dielectric and the air or solution between the periodic features. OD is the average optical density of the grating material,  $T$  is the thickness, and  $\theta$  is the Bragg angle. Although developed for a 1-D grating configuration, Eq. (3) illuminates the more general dependence of the DE on the real ( $n$ ) and imaginary ( $k$ ) components of the refractive index.

Using this methodology, Schanze and co-workers showed (with 1-D gratings) that varying either  $k$  or  $n$  while holding the other constant yields readily detectable changes in diffraction efficiency. Furthermore, in their experiment, the diffraction efficiency proved nearly 30 times more responsive to changes in the real component of the index of refraction than to changes in absorptivity [42]. This suggests that diffraction-based sensors might prove superior to absorption-based sensors in many instances.

The wavelength ( $\lambda$ ) dependent absorptivity ( $k$ ) and index of refraction ( $n$ ) are interrelated via the Kramers–Kronig relation [43,44]:

$$\Delta n(\omega') = \frac{c}{\pi} \int_0^\infty \frac{\Delta \alpha(\omega)}{\omega^2 - \omega'^2} d\omega \quad (4)$$

where  $\omega$  equals  $2\pi c/\lambda$ , and  $\alpha$  equals  $4\pi k/\lambda$  (in cm). Schanze and co-workers have illustrated the application of this relation to a simulated Gaussian change-in-absorptivity ( $\Delta k$ ) curve. Interestingly, the index of refraction increases to the red of the maximum in the  $\Delta k$  curve (where  $\Delta k$  is positive) and decreases to the blue [42]. It was also shown that if the sign of the perturbation ( $\Delta k$ ) is changed,  $\Delta n$  increases to the blue and decreases to the red of the change. Based on these results, an ideal material for diffraction-based sensing would be one that exhibits significant changes in the real refractive index in response to an analyte.

### 3.2. Electrochemical modulation of optical diffraction

A cyclic voltammogram of a PANI thin film is shown in Fig. 5a with the characteristic redox waves ( $E_{1/2} = 1.4$  and 4.5 V versus Ag | AgCl) demonstrating electrochemical changes occurring along the polymer chain with applied potential. Fig. 5b shows the electrochemically modulated absorption spectra for a PANI film. Absorbance values have been converted to absorptivity through use of literature values for  $k$  for PANI prepared in acidic chloride solutions [45,46]. At an applied potential of  $-0.2$  V, the PANI film exhibits a spectrum characteristic of the fully reduced leucoemeraldine form. Gradually increasing the applied potential to 0.30 V yields a progressive increase in absorbance near 800 nm. This absorption band is characteristic of the partially oxidized emeraldine PANI and, as seen in Fig. 5a, corresponds to the first oxidation of the film ( $E_{1/2} = 0.14$  V). At 0.40 V, a new absorbance band begins to grow in at 580 nm and dominates the spectrum by the time a potential of 0.60 V is achieved. At the same time the 800 nm band steadily disappears. This second absorbance change is characteristic of formation of the pernigraniline form of PANI and corresponds to the second electrochemical oxidation peak at  $E_{1/2} = 0.45$  V.

In Fig. 5c, the change in absorptivity for leucoemeraldine to emeraldine PANI is shown. This oxidation induces a significant  $\Delta k$  near 800 nm. Application of the Kramers–Kronig transformation to the absorption spectrum yields an index of refraction spectrum (real component) that features a decrease of 0.29 at 633 nm (see figure). The decrease in  $n$  should cause a decrease in the PCRI and therefore a decrease in DE. Fig. 5d illustrates the change in absorptivity accompanying further oxidation to the pernigraniline form. The Kramers–Kronig transformation of the second absorptivity change yields an increase in the real component of 0.482 at 633 nm. It is therefore expected that the PCRI and DE at the second oxidation potential will increase to values even greater than the completely reduced PANI film. Using the real refractive

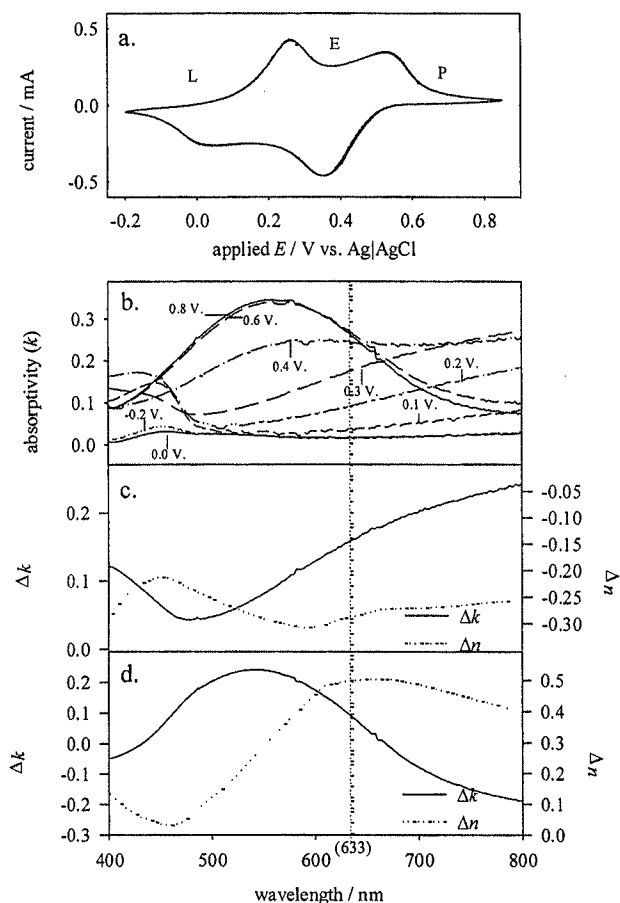


Fig. 5. (a) Voltammetric response of a typical PANI thin film immersed in a 0.1 M aqueous solution of HCl. L, E, and P correspond to leucoemeraldine, emeraldine, and pernigraniline PANI and indicate the predominant form as a function of applied potential. (b) Electrochemical modulation of the absorptivity spectra of PANI in acidic (pH 3) chloride solution. (c)  $\Delta k$  for the leucoemeraldine to emeraldine transition and the Kramers–Kronig transformation which gives the  $\Delta n$ . (d)  $\Delta k$  for the emeraldine to pernigraniline transition and the Kramers–Kronig transformation showing  $\Delta n$ .

index of 1.63 measured by Brudzewski and Grodzicka for reduced leucoemeraldine [47], the analysis yields real refractive indices for emeraldine and pernigraniline of 1.34 and 1.82, respectively, at  $\lambda = 633$  nm. The emeraldine value is in agreement with values from ellipsometry studies of PANI prepared in chloride solutions [46,47]. Very few studies have reported values for pernigraniline PANI, although the real refractive index has been observed to increase at higher positive potentials [48].

Shown in Fig. 6 are experimental examples of the electrochemical modulation of optical diffraction by a PANI grating. The behavior observed is fully consistent with the above predictions from the Kramers–Kronig relation. At the onset of the first oxidation, the intensity of the undiffracted beam ( $I_{0,0}$ ) decreases, as does the intensity of the first-order diffraction point ( $I_{1,1}$ ). The 7% decrease in intensity at  $I_{0,0}$  is attributed to the

electrochromism of the film as it absorbs a greater fraction of the incident light. (Note that the DE of a grating is directly proportional to the intensity of any of the diffracted beams, thus the variation of  $I_{1,1}$  provides a relative measure of DE). As noted, DE values are expected to be significantly more sensitive to changes in  $n$  than to changes in  $k$ ; the 55% decrease in  $I_{1,1}$  is due primarily to a decrease in the real refractive index which, in turn, reflects the growth of an intense absorbance band to the red of the probe beam. At the onset of the second oxidation of the film,  $I_{0,0}$  decreases slightly while  $I_{1,1}$  increases to nearly 130% of its fully reduced value.  $I_{1,1}$  increases at the second oxidation in accordance with the Kramers–Kronig transformation of the induced  $\Delta k$  at 580 nm. The increase in light diffracted is due to the increase in the PCRI of the PANI grating at 633 nm. The relative DE of the PANI grating therefore increases upon formation of this oxidation state.

### 3.3. Chemical modulation of optical diffraction

With the refractive index behavior of PANI characterized by electrochemical switching, we reasoned that this grating might also be capable of functioning as a crude chemical sensing device. It was expected that the

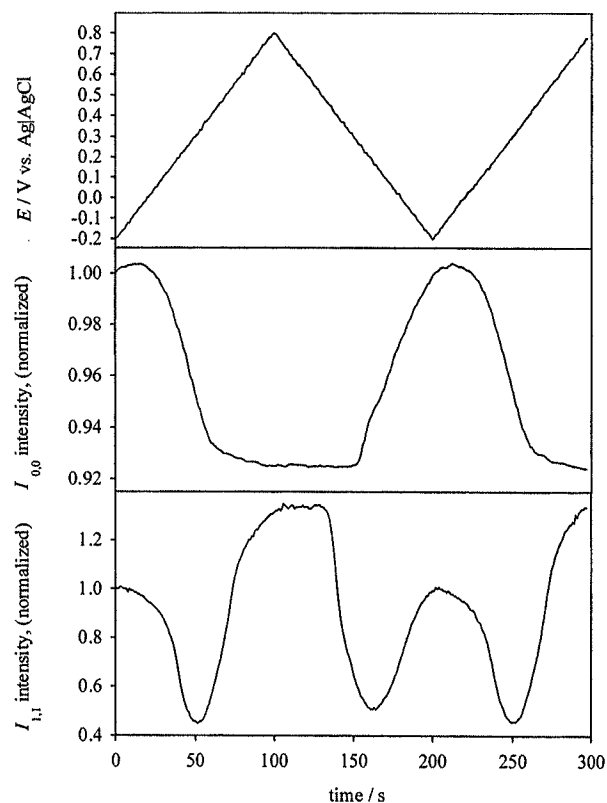


Fig. 6. Electrochemical switching of a PANI diffraction grating at a sweep rate of  $10 \text{ mV s}^{-1}$ .  $I_{0,0}$  and  $I_{1,1}$  represent normalized light intensities of the undiffracted beam and one of the first-order-diffracted beams, respectively.

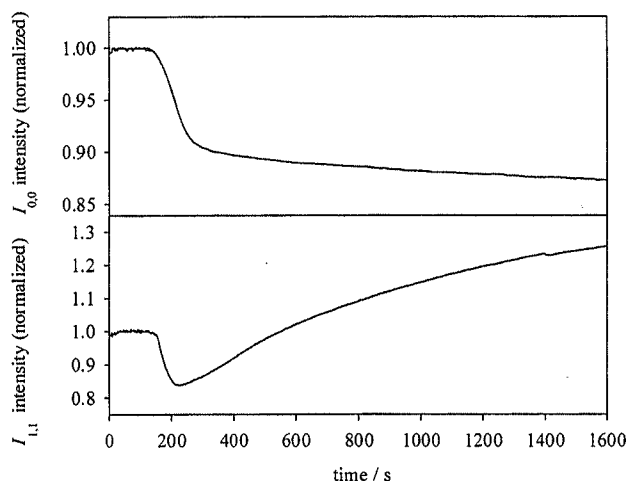


Fig. 7. Chemical switching of a PA diffraction grating with  $\text{Br}_2$  vapor.

film would exhibit different DE values in the absence and presence of a strong oxidant such as  $\text{Br}_2$ . Fig. 7 shows that the DE of a PANI grating responds as expected to  $\text{Br}_2$  vapor. Within 4 min,  $I_{0,0}$  and  $I_{1,1}$  drop by approximately 10 and 16%, respectively causing a decrease in DE. As with the electrochemical DE measurements, the decrease in  $I_{0,0}$  is attributed mainly to an increase in absorptivity, while the decrease in  $I_{1,1}$  is due primarily to a decrease in  $n$ . The pernigraniline oxidation state is fully realized in about 30 min ( $76 \pm 6$  ppm  $\text{Br}_2$ ) as indicated by the increase in DE due to the characteristic increase in refractive index. These preliminary results for the gratings are encouraging, both with respect to speed (seconds to minutes) and detection limit (ppm).

#### 4. Conclusions

The unique light absorbing behavior of PANI in its various oxidation states make this polymer a useful system for illustrating the interplay of the index of refraction and absorptivity of a material. The assessment of the relative diffraction efficiency of a periodic grating of PANI was shown to be a useful method of measuring electrochemically and chemically induced changes in the refractive index of the polymer. The DE of the fabricated gratings exhibits excellent Kramers–Kronig type behavior.

While no quantitative data concerning absolute diffraction efficiencies have been obtained, the results presented here give a qualitative picture of the fluctuations of the index of refraction of PANI. The chemical switching of these diffraction gratings provide some encouraging insight into the enhanced sensitivity which might be achieved through diffraction-based sensing.

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