Organic Electronics 37 (2016) 271–279

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Switchable diffractive optics using patterned PEDOT:PSS based electrochromic thin-films

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ARTICLE INFO

Article history:
Received 2 May 2016
Received in revised form
1 July 2016
Accepted 5 July 2016
Available online 15 July 2016

Keywords:
PEDOT:PSS
Electrochromic devices
Diffraction
Fresnel lens
Optics

ABSTRACT

We demonstrate switchable, thin film diffractive optical gratings and Fresnel zone plate lenses fabricated using a micro-patterned electrochromic polymer and gel electrolyte. Electrochemically switching the conductive polymer PEDOT:PSS causes the patterned layer to change between a low-absorption to high absorption state, acting as an amplitude diffractive optical element. The switchable lens and gratings were fabricated using a lithographically patterned electrochromic polymer, a gel electrolyte, and an ITO-coated glass substrate. Within an applied voltage of −1 V to 1 V, the diffraction efficiency of the switchable lens can be varied 4.1-fold between the 'on' and 'off' states. Due to their low actuation voltage and biocompatibility, electrochemically actuated diffractive optics have potential applications in low power and implantable biomedical devices.

1. Introduction

Organic and inorganic electrochromic (EC) materials have been used in electrochromic displays and attenuators for over four decades primarily due to ease of processing and cost [1–9]. EC materials reversibly change their absorption spectrum in response to a voltage-driven redox reaction. This effect has been implemented in a variety of devices, including switchable transparency windows ("smart glass") and displays [1,3,10,11]. The electrochromic effect is characteristically observed in response to an applied voltage as an ion exchange between the EC material and an electrolyte which changes the oxidation state of the EC material. The result is a voltage driven change in color of the material, as well as additional material property changes such as conductivity. EC materials include inorganic metal oxides such as WO_3, molecular pigments such as viologens and iron ferrocyanide (Prussian Blue) [1,4], and organic conductive polymers such as poly(3,4-ethylene-dioxythiophene) doped with poly(styrene-sulfonate) (PEDOT:PSS) [10,12,13]. Among conductive polymers, PEDOT:PSS is used extensively in the field of organic electronics and EC devices due to its chemical stability, flexibility, and relatively high conductivity of >1000 S/cm [14–17]. In the case of PEDOT:PSS, the electrochemical redox reaction will dope (oxidize) or dedope (reduce) the material thereby changing its conductivity and shifting its absorption spectrum from the infrared into visible wavelengths, which is observed as a darkening of the material. This shift can be exploited in applications that range from electrochemical displays to transistors [18,19]. EC materials such as PEDOT:PSS have intrinsic advantages over other thin-film optical materials such as liquid crystals (LCs), including low voltage DC actuation, ease of processing on flexible substrates, compatibility with both aqueous and organic electrolytes, and demonstrated biocompatibility [20–24]. The explicitly ionic electrochemical actuation mechanism of PEDOT:PSS also enables the materials to interface seamlessly with physiological environments [21,25,26]. Micro-patterned EC devices using amplitude diffraction grating structures have previously been used in EC devices to yield improved coloration efficiency [12,27,28], and recently a diffractive EC device was demonstrated using a 3D nanostructured conjugated polymer EC material, including a Fresnel zone-plate (FZP) lens [29]. However, characterization of the diffraction efficiency of such devices have not been perform, nor has such a system been demonstrated using simple and well understood EC systems such as PEDOT:PSS.

Using diffractive optics, elements such as Fresnel lenses can be

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http://dx.doi.org/10.1016/j.orgel.2016.07.004
1566-1199/

made using thin, planar patterns that focus light similar to traditional refractive lenses but have the added advantage of utilizing thin substrates to attain similar optical properties. Diffractive optics use spatially varying amplitude or phase modulation to interfere light and control the spatial distribution of the transmitted light beam. For example, an amplitude FZP lens can be generated from a structure of concentric rings of alternately low and high absorption segments with varying pitch without the volume and mass of material that would be needed to manufacture a similar refractive lens from conventional dielectric material. FZP micro-lens arrays on thin, flexible substrates have been used for wide-field imaging in bio-inspired compound eyes [30]. Fixed FZP lenses patterned on top of conventional refractive lenses have been shown to perform well as multifocal intraocular lenses (IOLs) for post-cataract surgery prostheses [31,32]. However, all of the FZP lenses in these studies feature fixed focal lengths and the lens power cannot be altered once fabricated. The ability to dynamically alter the focal length of an optical device by switching a diffractive optical element 'on' or 'off' using an external electrical signal would have significant applications for a range of optical devices such as lenslet arrays and switchable focus optics, including biomedical ophthalmic devices such as electrically switchable focus IOLs [33,34]. By combining the advantages of diffractive optics with active EC materials, a platform in which switchable diffractive optics with the ability to dynamically alter the focus of a lens can be developed. Patterned EC layers can be combined with traditional refractive optics to enable a device to repeatedly and reversibly switch the focal length of a lens in response to an electrical signal.

Although switchable diffractive elements for ophthalmic devices using phase modulating liquid crystals have been studied [33,34], the long-term biocompatibility of LCs along with the need to encapsulate the LCs so as to protect the immediate environment around the devices remains a concern [35]. Unlike LC materials that are generally incompatible with biological systems, PEDOT:PSS has a proven history of biocompatibility and devices made from PEDOT:PSS EC materials have been studied as *in vivo* biomedical devices [21–23,25,26,36–38]. In addition, LC based optical device might require complex voltage modulations and difficult processing conditions, while EC diffractive optics can be actuated using a low-voltage DC signal and are easily solution processed [1,2,4,13]. The ability to switch on-and-off a thin-film lens with a low DC voltage can be used to make varifocal contact and IOL devices, with the power supplied using a RF coil and rectifier, or a small on-board power source. A detailed study and characterization of the full potential of active diffractive optics (including diffraction efficiency) using biocompatible EC materials in aqueous electrolytes has been limited to-date.

In this work, we fabricate and characterize a PEDOT:PSS-based switchable opto-electrochemical device (OECD) that consists of an amplitude modulated diffractive optical elements, including FZP lenses and diffraction grating structures, in which the diffraction efficiency can be controlled as a function of the applied voltage. By utilizing the electrochromism of PEDOT:PSS, a FZP lens can be switched between a nearly uniform low absorption (oxidized) 'off' at state with infinite focal length, to a pattern of alternating low and high absorption (reduced) rings in the 'on' state with a finite focal length, as shown in Fig. 1a. The OECDs were fabricated by micropatterning a spin-coated EC layer of PEDOT:PSS on an ITO-coated glass substrate using conventional lithographic patterning. FZP lenses and amplitude diffraction gratings devices of different sizes were made to characterize the operation and diffraction efficiency. We show that the maximum intensity in the focus of a FZP lens can be changed by a factor of 8.2 with a voltage swing of 2 V, and a diffraction efficiency of up to 0.72%. We also examine the ultimate potential diffraction efficiency of OECDs and their potential as ophthalmic biomedical devices.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.orgel.2016.07.004.

2. Materials and methods

In PEDOT:PSS, the electrochemical ion exchange described below changes both the conductivity and the absorption spectrum of PEDOT [10,13,39]:

$$\mathrm{PEDOT}^{+}:\mathrm{PSS}^{-}+\mathrm{M}^{+}+e^{-}\rightarrow\mathrm{PEDOT}^{0}+\mathrm{M}^{+}:\mathrm{PSS}^{-}$$

where M^+ is a cation from the electrolyte, such as Na^+ or Li^+. In the ion exchange, PSS^- anions are displaced from their ionic bond with doped $PEDOT^+$, resulting in a dedoped (reduced) $PEDOT^{\circ}$ and low conductivity of the film. Due to this electrochemical redox reaction, polaron states within the electronic band structure of the semiconducting polymer are removed, increasing the band gap of PEDOT and making the material resonant with higher energy photons, increasing its absorption at visible wavelengths. This color change is exploited by a typical EC display or window which is a sandwiched structure consisting of a transparent electrode such as indium tin oxide (ITO) on glass or PET film, the EC material, an electrolyte and/or ion storage layer, and a second transparent or metallic counter electrode.

A schematic of a switchable FZP lens and a cross-section of an OECD are shown in Fig. 1. The spacing of the concentric ring structure in a FZP decreases as $1/r^2$ where r is the radial distance from the center of the lens. The alternatingly electrochemically active regions with switchable absorption and the chemically over-oxidized inactive regions diffract light at an angle inversely proportional to the ring spacing such that the incident light is diffracted to a single focal point. In binary FZPs, some of the light is diffracted into higher order modes as well, resulting in multiple foci. The power in higher order foci falls off proportional to m^{-2}, where m=1, 3, 5… is the mode order. To demonstrate proof-of-concept devices, the patterns for the binary FZP lenses in this paper were generated for lens powers of 1.5 and 3.0 diopters (focal lengths of 666 and 333 mm) [40]. Each lens has a diameter of 8 mm and was designed for an incident wavelength of 594 nm. The center circle was designed to be transparent while the spacing between the outermost rings is 25 μm and 50 μm for the 3.0 and 1.5 diopter lenses, respectively. FZP lenses of higher lens power (shorter focal length) can trivially be fabricated by altering the concentric ring spacing within the constraints of optical lithography. Additionally, linear diffraction gratings were fabricated as patterned lines of alternating inactive and active electrochromic regions. The gratings were designed with pitches of 10, 20, 30, and 40 μm, and a nominal duty cycle of 50%, defined as the ratio of the width of the active lines to the grating pitch.

2.1. Device fabrication

To fabricate the switchable OECD, ITO-coated 25 mm × 25 mm glass slides (Sigma-Aldrich) with a resistivity of 8–12 Ω/sq. were used as substrates. The coated slides were cleaned in soap solution, acetone, and isopropanol in a sonicator (Branson) and subsequently dried by blowing with N_2 gas. The EC solution consisted of PEDOT:PSS (Clevios PH-1000, Heraeus), 5 v/v % glycerol, 0.5 v/v % dodecylbenzenesulfonic acid (DBSA, Sigma-Aldrich), and 1 w/w % (3-glycidyloxypropyl)trimethoxysilane (GOPS, Sigma-Aldrich) and was spin-coated onto the substrate at 1000 rpm for 60 s. The presence of glycerol enhances the conductivity of the PEDOT:PSS formulation while the DBSA serves as a surfactant [41]. GOPS enhances the hydrolytic stability of the formulation and prevent