One Dimensional Photonic Crystals using Ultra-high Refractive Index Chalcogenide Hybrid Inorganic/Organic Polymers

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Supporting Information Placeholder

ABSTRACT: We report on the fabrication of wholly polymeric one dimensional (1-D) photonic crystals (i.e., Bragg Reflectors, Bragg Mirrors) via solution processing for use in the near (NIR) and the short wave (SWIR) infrared spectrum (1-2 μm) with very high reflectance (R ~ 90-97%). Facile fabrication of these highly reflective films was enabled by direct access to solution processable, ultra-high refractive (n) index polymers, termed, Chalcogenide Hybrid Inorganic/Organic Polymers (CHIPs). The high refractive index (n) of CHIPs materials (n = 1.75 - 2.10) allowed for the production of narrow band IR Bragg reflectors with high refractive index contrast (Δn ~0.5) when fabricated with low n polymers, such as cellulose acetate (n = 1.46). This is the highest refractive index contrast (Δn ~0.5) demonstrated for an all-polymeric Bragg mirror which directly enabled high reflectivity from films with 22 layers or less. Facile access to modular, thin, highly reflective films from inexpensive CHIPs materials offers a new route to IR Bragg reflectors and other reflective coatings with potential applications for IR photonics, commercial sensing and LIDAR applications.

The ability to control the propagation of light with a high degree of precision is integral for the fabrication of various optical devices that function in both the visible and infrared (IR) spectrum, such as sensors and light imaging and ranging (LIDAR) systems. One of the most basic optical constructs that allows for such control are Distributed Bragg Reflectors (DBRs) or, more broadly, 1D photonic crystals (1-D PC's). These reflective films are composed of alternating layers of disparate dielectric materials whose periodicities and differences in refractive index determines, respectively, the wavelength and magnitude of light reflected. The tunability and selectivity of these systems make them uniquely suited towards applications where low power loss light confinement is ideal, such as in microcavities[1] and solar cells[2]. DBR fabrication has been widely conducted via vapor deposition of metals or metal oxides due to the high uniformity of thin films and the high refractive index that allows for high reflectivity to be achieved for a low number of layers. Hence, fabrication of Bragg mirrors has been conducted using high n metal oxides (TiO_2 (n = - 2.48))[3], various semiconductors[4] and chalcogens (tellurium (n = 4.80)[5]) in conjunction with low n materials like SiO_2 (n = 1.44)[6] to generate high refractive index contrast (Δn = 0.5 – 3.0) and enable high reflectivity for only a few layer pairs. However, the fabrication of all-polymeric, highly reflective 1D-PCs via solution processing remains an important challenge, particularly in the IR spectrum.

An importance technological challenge that remains for the fabrication of highly reflective, thin, wholly polymeric DBRs is the creation of high refractive index contrast (Δn) between the polymer layers. The vast majority of engineering plastics typically exhibit refractive indices in the range of n = 1.45 to 1.65 which ultimately limits the refractive index contrast that can be generated for DBRs. The limitations of low Δn with conventional synthetic polymers has led to the development of polymer chemistry and engineering solutions that enable a large number of layers to be rapidly processed to create high reflectivity films. The engineering challenges associated with fabrication of all polymeric DBRs with low Δn was demonstrated in the seminal work of Miyamoto et. al.[7] requiring a custom built, automated spin coater to fabricate 170 alternating layers of polystyrene (n = 1.582) and poly vinyl alcohol (n = 1.527) (Δn = 0.055) in order to achieve nearly 100% reflectivity at ~600 nm. When such a large number of layers is necessary, spin coating processes for DBRs becomes more

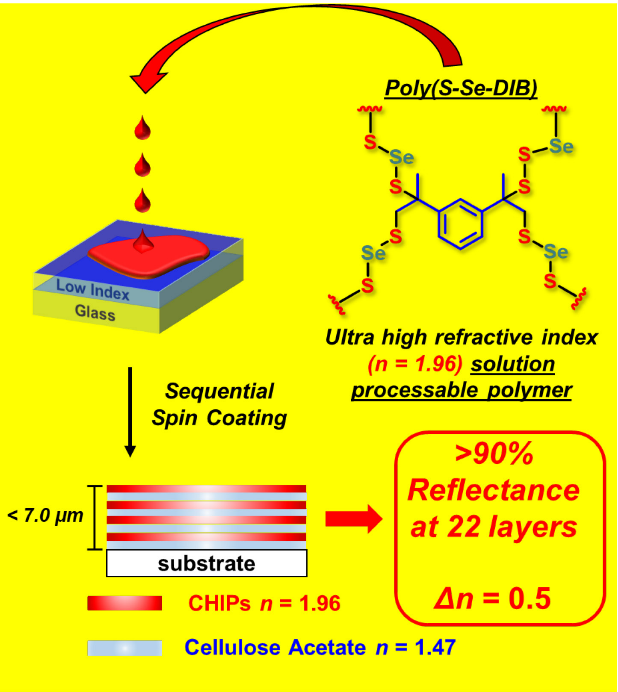

Figure 1: General scheme for the fabrication of highly reflective all polymer Bragg reflectors from CHIPs materials that possess tunable reflectance across the NIR and SWIR (**1.0-2.0 µm**)

challenging as control over thin (<500 nm) films becomes difficult to achieve with high fidelity[8] and has been shown to lead to changes in the peak reflectance of the DBR[9]. Melt extrusion of multilayer polymer films for optical applications has been extensively developed (both industrially and academically) to enable fabrication of highly reflective all polymer DBRs using commercial thermoplastic materials.[10,11] Self-assembly of block copolymers (BCPs) into microphase separated thin films with lamellae morphologies were fabricated by Thomas et. al.[12] in order to process DBRs as a route to preparing DBRs, as hundreds of layers can be assembled all at once. This concept of BCP self-assembly was revisited by Grubbs and Atwater by the use of bottle brush block copolymers to create microphase separated films exhibiting periodicities of the lamellar domains that allowed for reflection further into the near-IR (NIR)[13]. The selective inclusion of high *n* metal oxide[14,15], semiconductor[16], and even noble metal[17] nanoparticles as additives in self assembled DBRs has also been explored in attempts to increase the dielectric contrast of each layer. However, the concept of using solution processable polymers possessing very high *n* has not been widely explored.

Inorganic porous metal oxide 1-D PCs have been fabricated via templated solution processing multi-layers[18-20], along with spin coating of discrete nanoparticles[21,22] to achieve high refractive index contrast and high reflectivity using only a few layers of alternating dielectric materials. However, technical challenges persist to process mechanically robust DBRs with these inorganic materials, particularly for larger scale production using solution processing methods.

Conversely, wholly polymeric DBR systems are inherently more amenable to large scale roll-to-roll solution processing methods but remains limited by access to inexpensive, high refractive index polymers to achieve high refractive index contrast. Early reports on such systems used commercially available organic polymers based on cellulose acetate and poly(N-vinylcarbazole)[9,23-25] to fabricate polymer DBRs with Δ*n* = 0.2. In order to further increase the refractive index contrast in DBRs, Comoretto and Voit et. al. prepared a novel hyperbranched polyvinylsulfide (*n* = 1.7) that allowed for a higher Δ*n* = 0.3[25]. Inclusion of inorganic nanoparticles into spun coat layers of polymer composites have been demonstrated by both Comoretto[14,26] and Watkins[27,28] where Δ*n* = 0.34 in DBRs with sufficiently high nanoparticle loadings (70%)[27]. These seminal reports point to the potential to fabricate reflective, thin polymeric DBRs using solution processing methods, however, the ability to create high refractive index contrasts comparable to the more reflective and thinner inorganic systems, remains an important challenge.

Herein we report on the fabrication of wholly polymeric 1D photonic crystals *via* spin coating that achieve greater than 90% reflectance at just 22 layers. Furthermore, the peak reflectance was shown to be tunable across the NIR and SWIR spectrum. The key to preparing these devices was synthetic access to Chalcogenide Hybrid Inorganic/Organic Hybrid Polymers (CHIPs)[29-32] containing a high content of selenium and sulfur units which impart ultra-high refractive index to the polymer material ($n \leq 2.1$) that was also readily solution processable (**Fig. 1**). Using CHIPs as the high index layer in an all polymer Bragg reflector, a high refractive index contrast (Δ*n* = 0.5) was achieved when cellulose acetate was used as the low *n* layer. This represents the highest index contrast generated for a wholly polymeric Bragg reflector and enabled the remarkable reflectivity observed in these solution processed thin films.

We have previously demonstrated the ability to synthesize high refractive index (*n* = 1.75-1.85) polymers by copolymerization of organic monomers with elemental sulfur via a process termed *inverse vulcanization*[32,33]. Most recently, we have expanded the scope of this polymerization technique to allow for incorporation of selenium atoms to prepare poly(sulfur-*random*-selenium-*random*-(1,3-diisopropenyl-benzene) (poly(S-*r*-Se-*r*-DIB) terpolymers which has allowed access to solution and melt processable synthetic polymers with refractive indices up to *n* = 2.1[30]. The *inverse vulcanization* process utilizes the homolytic ring opening polymerization of sulfur above its floor temperature of 160 °C to generate sulfuryl radicals that readily copolymerize with both elemental selenium (i.e., grey polymeric Se) and organic, vinylic comonomers. See Supporting Information and Figures **S7** and **S9** for more detailed information on poly(S-*r*-Se-*r*-DIB) molar mass and T_g. An attractive feature of the inverse vulcanization process is the ability to modulate the refractive index and solubility of CHIPs materials by controlling the organic comonomer feed ratios. This unique feature of CHIPs materials is useful in the fabrication of Bragg reflectors as the ability to select the desired *n*, and hence refractive index contrast, allows for control over the optical bandgap of the assembled Bragg reflector in addition to wavelength of reflection.

To demonstrate the advantage of fabricating polymer DBRs possessing high refractive index contrast (Δ*n* = 0.5) computation simulations of the reflectivity (with Essential Macleod thin film software) were conducted on two different Bragg reflector systems: cellulose acetate (*n* = 1.47) with polycarbonate (*n* = 1.57) (a commonly used high refractive index polymer) and cellulose acetate paired with a CHIPs material (*n* = 1.96) (**Fig. 2a**). These simulations reveal that only 10 bilayers are needed to achieve greater than 95% reflectance for DBRs possessing a Δ*n* = 0.5 with CHIPs as the high index layer, while DBRs fabricated with the polycarbonate as the higher *n*

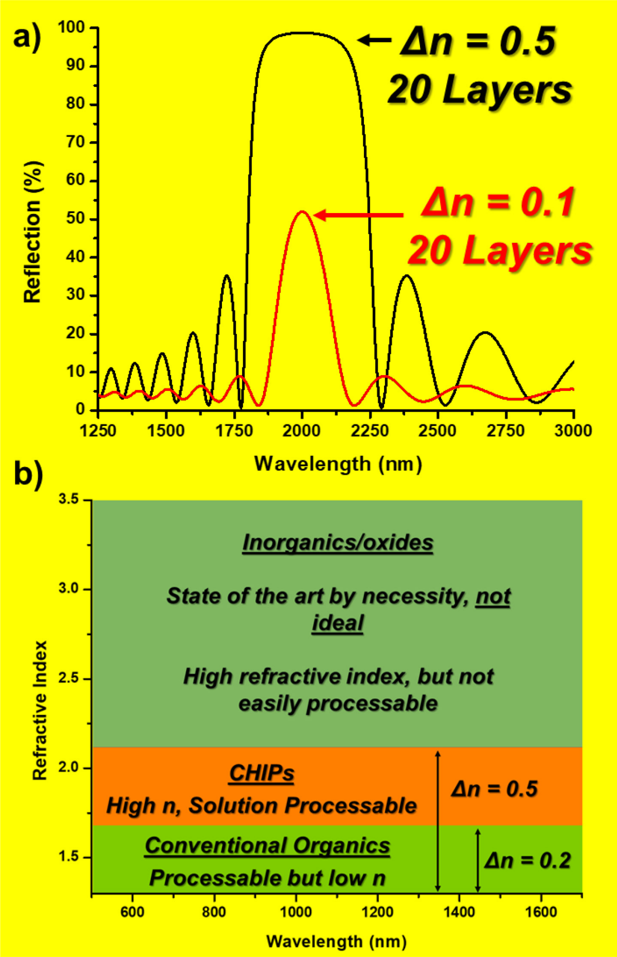

Figure 2: a) Simulated reflectance of all polymer Bragg reflectors fabricated from CHIPs/cellulose acetate pairs (black line) and polycarbonate/cellulose acetate pairs (red line) and **b)** Schematic representation of the Δ*n* values that can be generated using various classes of materials

material only achieved less than ~50% reflectance at the same number of bilayers, illustrating the unique benefit CHIPs offer for the efficient fabrication of all polymer Bragg reflectors by spin coating. While DBRs with even higher refractive index contrasts can be generated by using inorganic materials, as has been previously discussed, the use of CHIPs enabled entry for the first time to inexpensive, polymeric, highly reflective films amenable to spin coating or solution processing (**Fig. 2b**).

For the fabrication of CHIPs based Bragg reflectors, a modified method from Commerto and Voit et. al.[25] was employed which demonstrated the use of aromatic solvents to dissolve the higher *n* polymer paired with cellulose acetate solutions in diacetone alcohol to deposit films with orthogonal solubilities. CHIPs materials were found to be soluble in aromatic solvents, particularly chlorobenzene and toluene. To this end, cellulose acetate was dissolved in diacetone alchohol and the CHIPs (poly(S_{50}-*r*-Se_{20}-*r*-DIB_{30}) terpolymer (where the subscripts denote feed ratios and whose composition was selected for a balance between solubility and high refractive index) was dissolved in chlorobenzene and diluted with toluene as needed for the processing of thinner layers. Peak reflection (λ) in a Bragg reflector was tuned for a given system by varying the thicknesses of the two layers in the reflector according to **Equation (1)**,

$$t_H = \frac{\lambda}{4n_H} \quad t_L = \frac{\lambda}{4n_L} \qquad \textbf{Equation (1)}$$

where *t* represents thickness in nm, *n* is refractive index and *H* and *L* denote “high” and “low” index components, respectively. Using this equation, spin curves were assembled in order to target 1.0, 1.5, and 2.0 μm peak reflectivity (see supporting information for details of film thickens design and fabrication for DBRs at each wavelength).

CHIPs based Bragg reflectors designed for reflection at 1.0, 1.5 and 2.0 microns were characterized via optical transmission and polarized incident angle resolved reflectance measurements to confirm the fabrication of uniformly coated films of high reflectivity at the targeted wavelengths. Reflectance (R) values for these CHIPs DBRs were initially determined via measurement of the optical transmission (T) from 350 to 3000 nm (R = 100-T) which confirmed good agreement of the measured peak reflection wavelength (**Fig. 3**) with targeted values from simulations (**Fig. 2a**). More strikingly, reflectance values of greater than 90% were observed for these solution processed CHIPs DBRs at 22 layers (**Fig. 3**). Furthermore, reflectance values up to 97.5% were also demonstrated by the addition of 3 more bilayers (see Supporting information Figure **S2**). Direct reflectance measurements of these CHIPs DBRs also confirmed similar levels of reflectivity (see supporting information Figure **S3**). To confirm the solution deposition of uniform films, transmission measurements of all three CHIPs DBRs were conducted in four different locations across the entire ~2 cm² film where neither the magnitude nor λ_{max}

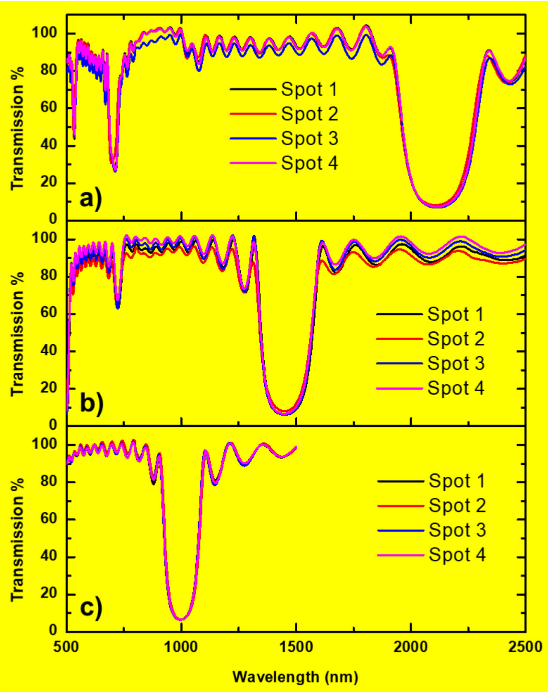

Figure 3: Transmission spectra recorded in various spots on ~2 cm² Bragg reflectors with 22 layers each: **a)** ***92.6%*** calculated reflectance at ***2113 nm*** **b) 93.8%** calculated reflectance at **1450 nm c) 93.2%** calculated reflectance at **998 nm**

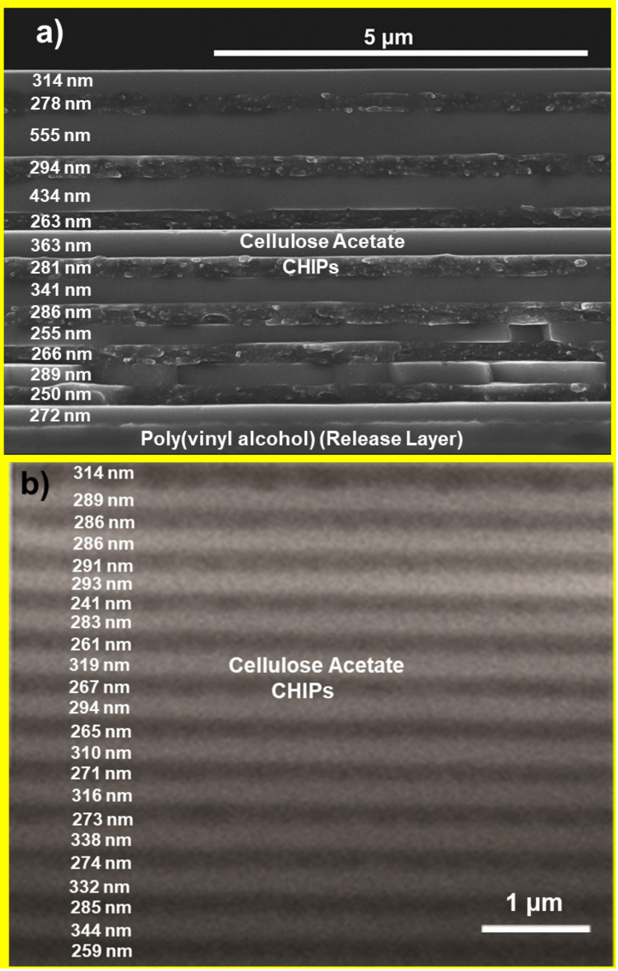

Figure 4: a) SEM image of a representative multi-layered film (15 layers) from CHIPs and cellulose acetate fabricated via spin coating and delaminated for imaging from a glass substrate with a PVA release layer designed for reflection at 2.0 µm **b)** SEM image of a representative multi-layered film (25 layers) from CHIPs and cellulose acetate fabricated via spin coating and delaminated for imaging from a glass substrate designed for reflection at 2.0 µm; both Bragg reflectors had targeted thickness of 260 nm and 340 nm for the CHIPs and Cellulose Acetate layers respectively

of these reflections were discernibly different for any given region of the sample, indicating good control over device fabrication. To further interrogate the quality of the Bragg reflectors produced, each sample was analyzed by polarization and angular dependent reflectivity (see supporting information **S4-S6**). For all DBRs, a shift in peak reflectance to shorter wavelengths was observed for both *s* and *p* polarizations; whereas the photonic band gap (PBG) with increasing angle of incidence for *p* polarized light was observed to shift to longer wavelengths, the PBG for *p* polarized light was largely unchanged as expected for classic DBRs[25]. Additionally, peak reflectance was measured to decrease with *p* polarized light while *s* polarized light resulted in marginally higher peak reflectance values and a concomitant decrease in background transmission, again, as would be expected by theory[25].

The layered film morphology of the assembled Bragg reflectors was confirmed by cross-sectional SEM imaging of both freeze-fractured and focused ion beam (FIB) milled interfaces. Initial SEM imaging was conducted of freeze-fractured multi-layered (See supporting information for sample preparation and imaging conditions) which revealed the presence of well-defined, layered morphology of CHIPs and cellulose acetate films indicating the sequential spin coating protocol employed does not disrupt the interface due to dissolution by the depositing solvent. Furthermore, the domains were determined to have periodicities commensurate to the nominal thicknesses targeted, which indicated good control over device fabrication. However, due to the potential for mechanical damage along these interfaces due to the freeze-fracture, FIB milling (with a gallium ion source) was also conducted of free standing Bragg reflectors to more accurately interrogate the homogeneity of thin film morphology at each interface from the spin coating process. Cross-sectional analysis of these FIB milled samples revealed the fabrication of highly uniform alternating layers of poly(S-*r*-Se-*r*-DIB) and cellulose acetate in much closer agreement to theoretical design targets from the computations simulations (see Supporting Information).

In conclusion, we have demonstrated for the first time, fabrication of highly reflective all polymer Bragg reflectors from the highest refractive index contrast attained in such a system ($\Delta n = 0.5$). This allowed for >90% reflectance at just 22 layers of alternating CHIPs and cellulose acetate easily assembled via spin coating and tunability over the NIR and SWIR. This seminal demonstration highlights the advantages of using these high refractive index polymers for IR optical applications and opens new possibilities for the fabrication of ultra-thin, broadband, IR reflective coatings.

ASSOCIATED CONTENT

Supporting Information

Experimental details for the preparation and characterization of sulfur copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare the following competing financial interests: Professor Pyun is the co-founder of Innovative Energetics, which is a company focused on sulfur materials developed for Li-S batteries.

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Committee and is managed by a Financial Conflict of Interest Management Plan.

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