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ABSTRACT

In this paper we present our current research in exploring a DNA biopolymer for photonics applications. A new processing technique has been adopted that employs a modified soxhlet-dialysis (SD) rinsing technique to completely remove excess ionic contaminants from the DNA biopolymer, resulting in a material with greater mechanical stability and enhanced performance reproducibility. This newly processed material has been shown to be an excellent material for cladding layers in poled polymer electro-optic (EO) waveguide modulator applications. Thin film poling results are reported for materials using the DNA biopolymer as a cladding layer, as are results for beam steering devices also using the DNA biopolymer. Finally, progress on fabrication of a Mach Zehnder EO modulator with DNA biopolymer claddings using nanoimprint lithography techniques is reported.

Keywords: DNA, Electro-optic modulator, waveguide, poled polymers, biopolymer

1. INTRODUCTION

Since its introduction as a material for photonic applications almost a decade ago, the marine-derived DNA biopolymer has been demonstrated in a wide range of devices including organic light emitting diodes (OLEDs), organic field effect transistors (FETs), and polymer EO modulators [1]-[6]. In many of these applications, a significant increase in performance has resulted from incorporating the DNA biopolymer in the device design due to its unique electronic and optical properties[7]-[9]. These unique properties make the DNA biopolymer well-suited for use as a conductive cladding material in polymer EO waveguide modulators. A DNA biopolymer formed from DNA and the surfactant hexadecyltrimethyl-ammonium chloride (CTMA) has been proposed as a potential conductive cladding material due to a combination of its low optical loss (0.2 dB/cm at 1310 nm) and relatively low electrical resistivity ($10^8$ Ω-cm at 90°C) [10]-[12]. Previous studies have demonstrated high poling efficiency using the DNA biopolymer as a cladding layer; however, the results reported have all been thin film EO coefficients and not in-device EO coefficients [13].

This paper will review recent changes to the processing technique of the DNA biopolymer and discuss the resulting performance enhancements of DNA biopolymer waveguide devices due to the removal of the ionic contaminants. This newly processed material has shown significant device stability and enhanced poling efficiency for EO poled polymer waveguide applications. These applications include thin film poling experiments, beam steering devices, and a Mach Zehnder EO modulator. Progress on these applications will be discussed.
2. PROCESSING

The DNA used in this study was derived from salmon roe and milt sacs obtained from waste products of the Japanese fishing industry and purified by researchers at the Chitose Institute for Science and Technology [1],[2]. Upon receipt, the DNA is sonicated to a mean molecular weight of 200 kDa and precipitated with the CTMA surfactant complex to provide greater molecular stability and make the DNA water insoluble. The resulting DNA-CTMA complex is what is referred to here as the DNA biopolymer. While a detailed description of the DNA-CTMA processing technique can be found in prior publications [14], a significant modification to the processing technique has been recently employed in the preparation of the DNA-CTMA [15]. This technique greatly improves the material properties and performance of the DNA biopolymer and the details have been described in a manuscript currently submitted for publication.

Briefly, the removal of the excess CTMA and NaCl (from the ion exchange reaction) is achieved using a combined soxhlet-dialysis (SD) method. In a typical dialysis process, small solutes diffuse from a high concentration solution to a low concentration bulk solvent across a semi-permeable membrane until equilibrium is reached. The preferred molecular separation depends on the selection of the membrane pore size. Frequent refreshing of the solvent outside the membrane ensures a higher efficiency of the dialysis process; however, for the quantities used in DNA-CTMA rinsing this also generates excessive amounts of solvent waste. To address this issue, Anyanwu et al. developed a semi-continuous flow dialysis technique using a soxhlet extractor, replacing the thimble with dialysis tubing [16]. By taking advantage of the high separation efficiency of the dialysis method and the semi-automation of the soxhlet apparatus, the combined SD process has been employed as an efficient and effective rinsing technique for the DNA-CTMA material.

![NMR spectra of DNA-CTMA with various rinsing techniques compared to CTMA. The main peaks are labeled directly below each spectrum. These data show no residual CTMA in the SD, 32 cycle rinsed DNA-CTMA [15].](image-url)

A qualitative analysis of the remaining unprecipitated CTMA present after the SD rinsing process was done using Nucleic Magnetic Resonance (NMR) spectroscopy. In these studies, 3-(Trimethylsilyl)-1-propane sulfonic acid-d6 sodium salt (DSS) was used as an internal reference proton compound. A solution of 5µL of DSS dissolved in D$_2$O at 2.5 mg/mL was added to each NMR sample. The control sample was a 0.05 mM CTMA solution in D$_2$O. The DNA-CTMA NMR samples were prepared by mixing 15 mg of DNA-CTMA in 1 mL of D$_2$O; they were left to sit overnight to allow any unbound CTMA to fully dissolve in the D$_2$O and the solid content was removed using a centrifuge. Three
DNA-CTMA samples were compared to the CTMA only solution: a DNA-CTMA solution prepared with the water-only rinsing technique (Heckman et al.) [14] and two DNA-CTMA solutions prepared with the SD rinsing technique for varying cycle lengths. The NMR results are in Figure 1 and show the presence of excess CTMA in the water-only rinsed sample, and the absence of all excess CTMA impurities in the SD rinsed DNA-CTMA after 32 SD rinsing cycles. The multiple large peaks in the NMR of the SD rinsed DNA-CTMA are attributed to residual EtOH.

3. THIN FILM POLING

The DNA biopolymer formed from DNA and CTMA has been proposed as an ideal conductive cladding material due to a combination of its low optical loss (0.2 dB/cm at 1310 nm) and low electrical resistivity (108 Ω/cm at 90 °C). The need for conductive cladding materials in polymer EO modulators has been recognized as necessary to achieve high poling efficiency in polymer modulator devices [17],[18]. However, many of the current cladding materials used in these devices are either not conductive with respect to the core layer or are made conductive through doping at the expense of increased optical loss. It is challenging to identify a cladding material with both low optical loss and sufficiently high conductivity to achieve good poling efficiency.

Previous studies involving the use of a DNA biopolymer as a conductive cladding layer were done with either a crosslinked DNA biopolymer that had significantly increased optical losses due to the crosslinking process, or were done with poorly performing core materials unsuitable for real-world device applications [7],[11],[12]. Additionally, our own work using the DNA biopolymer cladding layer was done with DNA that had been rinsed using the water-only method and not the SD rinsing technique [13]. While the results from that study were promising and the relative poling efficiency for the APC/CLD1 EO polymer was 96%, we were unable to achieve consistent poling results with other EO polymers. Since switching to the SD rinsed DNA biopolymer, however, we have been able to consistently achieve close to 100% relative poling efficiency with a wide variety of EO polymer materials. This has been achieved with very little electrode bubbling or electrical shorts as were common with the water-only rinsed DNA biopolymer.

The DNA biopolymer film was fabricated as described in detail in previous publications [13]. For this thin-film study, two-layer films were prepared on ITO substrates coated with a 50nm layer of TiO₂ for poling stability. Next, a 2 µm thick cladding layer was deposited, followed by a 2 µm thick EO polymer, and an 80 nm layer of gold was deposited on top. EO polymers used for this study were APC/CLD1 that was obtained from a private source and SEO100 and SEO110 that were purchased from Soluxra and prepared according the manufacturers specifications. The biopolymer cladding performance for each is directly compared to that of UV15, a commonly used cladding material for polymer modulator applications [19],[20]. The EO coefficient $r_{33}$ was measured at 1310 nm using a modified Teng and Man technique that takes into account the presence of the cladding material [21],[22]. The results from this study are summarized in Table I. For all three EO polymers studied, the DNA biopolymer consistently achieved nearly 100% relative poling efficiency (with respect to the poled EO polymers without a cladding material), while UV15 was consistently closer to 50%.

Table I. Data summary comparing the poling results between DNA-CTMA and UV15 bottom cladding layers with EO polymer core materials. Results were measured at 1310 nm.

<table>
<thead>
<tr>
<th>Core material</th>
<th>Cladding material</th>
<th>$r_{33}$ (pm/V)</th>
<th>Relative Poling Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>APC/CLD1</td>
<td>None</td>
<td>45</td>
<td>-</td>
</tr>
<tr>
<td>APC/CLD1</td>
<td>DNA-CTMA</td>
<td>43</td>
<td>96%</td>
</tr>
<tr>
<td>APC/CLD1</td>
<td>UV15</td>
<td>23</td>
<td>51%</td>
</tr>
<tr>
<td>SEO100</td>
<td>None</td>
<td>167</td>
<td>-</td>
</tr>
<tr>
<td>SEO100</td>
<td>DNA-CTMA</td>
<td>166</td>
<td>99%</td>
</tr>
<tr>
<td>SEO100</td>
<td>UV15</td>
<td>72</td>
<td>43%</td>
</tr>
<tr>
<td>SEO110</td>
<td>None</td>
<td>140</td>
<td>-</td>
</tr>
<tr>
<td>SEO110</td>
<td>DNA-CTMA</td>
<td>142</td>
<td>&gt;100%</td>
</tr>
<tr>
<td>SEO110</td>
<td>UV15</td>
<td>80</td>
<td>57%</td>
</tr>
</tbody>
</table>
4. EO BEAM STEERING DEVICE

While the thin film results using the DNA biopolymer as a cladding layer are a promising indicator of its suitability as a material for EO waveguide devices, a better indicator is its performance in an EO waveguide device. An EO waveguide beam steering device was designed; although performance was limited to DC testing and not high frequency [23]. The EO beam steering device described here is similar to the one reported by Sun et al. and is based on the concept that the propagation direction of a laser beam can be changed by applying an electric field to the EO medium to induce a change in refractive index [24]. The light propagates in the core layer of an EO polymer waveguide and when a DC bias voltage \( V_B \) is applied to a triangular top “prism” electrode, a triangular variation \( \Delta n \) in the refractive index of the core layer is induced according to Eq. (1):

\[
\Delta n = \frac{1}{2} n^3 r_{33} \frac{V_B}{d}
\]

where \( n \) is the refractive index of the core material with no applied field, \( r_{33} \) is the EO coefficient of the core layer, \( V_B \) is the applied DC bias voltage, and \( d \) is the thickness of the core layer. The laser beam is then deflected according to Snell’s Law in the same manner a beam of light is deflected through a prism [25].

![Diagram of the triangular top electrode and the deflection angle](image_url)

Figure 2. (a) Diagram of the triangular top electrode showing the incident beam in the planar waveguide, and the direction of deflection when the index increases by \( \Delta n \). (b) Diagram showing the definition of the effective deflection angle \( \theta_{eff} \) and its relationship to the beam displacement \( y \) at a distance \( L \) from the first deflection point [23].

In this work, a single triangle is used as the top electrode as shown in Figure 2. The height and the base width of the triangle are denoted by \( h \) and \( w \), respectively. The angle of incidence with respect to the top electrode is denoted by \( \theta_{inc} \) and is set to 30° for this work. The first and second deflection angles that occur at the entrance and exit of the triangle electrode “prism” are denoted by \( \theta_1 \) and \( \theta_2 \) respectively. The direction of deflection depends on whether \( \Delta n \) is positive or negative when a bias voltage is applied; for this work \( \Delta n \) is positive and the direction of deflection is shown in Figure 2 (a). If the displacement \( y \) of the beam from its original path is measured at a distance \( L \) from the first deflection point, the effective deflection angle \( \theta_{eff} \) can be expressed as \( \theta_{eff} = \tan^{-1} \frac{y}{L} \). The definition of \( \theta_{eff} \) is represented graphically in Figure 2 (b). If the beam is positioned to pass close to the tip of the electrode, then \( L >> w \) and \( \theta_{eff} \approx \theta_2 \). Using Snell’s Law, the deflection angle can then be expressed as:
\[ \theta_{\text{eff}} \approx \theta_2 = \sin^{-1}\left\{ \frac{n'}{n} \sin\left[2\theta_{\text{inc}} - \sin^{-1}\left(\frac{n}{n'} \sin \theta_{\text{inc}}\right)\right] \right\} - \theta_{\text{inc}} \]  

(2)

where \( n' = n + \Delta n \), and \( \Delta n \) is given in Eq. (1).

The beam steering device demonstrated a deflection efficiency of 99 mrad/kV and an in-device EO coefficient of 124 pm/V at 1550 nm. According to the manufacturer’s specifications, the expected thin-film value of \( r_{33} \) for SEO100 at 1550 nm is 110 pm/V for a poling field of 100 V/\( \mu \)m. The DNA biopolymer cladding layers, therefore, provide greater than 100% relative poling efficiency for the SEO100 material and at a reduced poling field of 75 pm/V. A similar device that used UV15 as the bottom cladding layer and the DNA biopolymer as the top cladding layer (necessary due to lack of orthogonal solvents between UV15 and the core) yielded a deflection efficiency of 34 mrad/kV and a corresponding in-device \( r_{33} \) of 43 pm/V was measured.

![Image](https://example.com/image1)

Figure 3. (a) IR image with room illumination of the device under test. (b) IR image in the dark showing a bright spot at the cut. (c) Magnified view of the bright spot [23].

5. MACH ZEHNDER EO MODULATOR

While the beam steering device is a good demonstration device, it is still a slab waveguide structure. A better structure for demonstrating a material’s suitability for EO waveguide applications is a patterned waveguide device such as a Mach Zehnder modulator. This has been an elusive goal for the DNA biopolymer due in large part to its inability to withstand common clean room fabrication processes necessary for forming the Mach Zehnder structure such as photolithography, chemical etching, and dicing.

Recent progress toward this goal has been made by using nanoimprint lithography (NIL) to directly stamp waveguide features into the DNA biopolymer. NIL is a non-optical method of pattern transfer that was developed as a cost-effective means of reproducing patterns otherwise only achievable through electron beam lithography or other more expensive or time-consuming processes [26],[27]. The nanoimprinter was a Nanonex NX-2600, which uses a flexible membrane system to transfer patterns from a rigid stamp into the material. The stamp was fabricated using photolithography on an SiO\(_2\) substrate and was coated with a release coating of chlorosilane Nanonex NXT-130 release agent prior to use to prevent the stamp from adhering to the DNA biopolymer during the imprint process.

![Image](https://example.com/image2)
A ridge waveguide structure was successfully imprinted into the DNA biopolymer and is shown in Figure 4. The imprint procedure begins with heating the film above its glass transition temperature to a temperature of 120-150 °C, next the stamp is applied at a pressure of 500 psi for 5 min. After 5 minutes, the sample is cooled and the stamp is released. After the imprint into the DNA biopolymer bottom cladding layer, a core layer and top cladding layer are subsequently spin coated on top. Laser light at 1550 nm has been successfully coupled into the imprinted waveguide channel. Thus far, only straight line, ridge waveguide structures have been imprinted, Mach Zehnder structures are planned to be printed in the near future.

![Figure 4. Ridge waveguide structure in DNA-CTMA imprinted with nanoimprint lithography techniques.](image)

**6. CONCLUSIONS**

Improvements in DNA processing have led to a photonics biomaterial with fewer impurities and better performance as a cladding material for EO polymer waveguide applications. Enhanced poling efficiency with a wide variety of polymer core materials was demonstrated using the DNA biopolymer as the cladding material compared to the UV15 cladding material. A slab waveguide beam steering device was demonstrated using the DNA biopolymer as the cladding layer with better performance than a similar device using UV15 as the cladding material. Nanoimprint lithography has been shown to be promising fabrication technique for patterning waveguide devices using the DNA biopolymer. A ridge waveguide structure has been directly imprinted into a DNA biopolymer thin film and 1550 nm laser light has been successfully coupled into it.

**REFERENCES**


