The fiber electric double layer platform for phase shifter based on Pockels effect of liquid molecules

MENG LUO,[1] DANHENG GAO,[1] XINGHUA YANG, [1,*] NIGEL COPNER,[2] ZHIHAI LIU,[1] XINGYUE WEN,[1] KANG LI,[2] AND LIBO YUAN,[1,3]

[1]*Key Lab of In-Fiber Integrated Optics, College of Physics and Optoelectronic Engineering, Harbin Engineering University, Harbin 150001, China*
[2]*Wireless & Optoelectronics Research & Innovation Centre, Faculty of Computing, Engineering & Science, University of South Wales, Wales, CF37 1DL, UK*
[3]*Photonics Research Center, Guilin University of Electronics Technology, Guilin 541004, China*
**Corresponding author: yangxh@hrbeu.edu.cn*

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The electric double layer was formed at the interface of electrode and liquid and has been widely used in a series of applications ranging from batteries to biosensors based on the electrical properties change. In this letter, we demonstrate a simple microfiber phase shifter based on the Pockels effect of liquid in the electric double-layer. By constructing an electric double layer around the microfiber, the phase shifter can be achieved. Furthermore, the effects of ion concentration and molecular polarity of liquids on this phase shifter were studied. The fiber electric double layer platform has the advantages of low voltage modulation and simple fabrication, which has the potential for wearable sensing devices, biopotential detection, and biomolecule detection.

In the past century, the study of electric double layer (EDL) has not diminished over time [1-3]. On the contrary, as the research progresses, the researchers become more convinced of its importance. For electrochemical analysis, the discussion of EDL is unavoidable [4]. For semiconductor sensors, the thickness of the EDL is determined as a thin layer with a thickness of several tens of nanometers at the interface of electrode and electrolyte, which is also very consistent with modern nano-semiconductor technology and opens the way for its applications [5, 6]. At present, a series of devices based on the electrical property changes in the EDL have been demonstrated, such as the microfluidic capacitive sensor [7], an EDL field-effect-transistor (FET) biosensors [8], and EDL-gated FET-Based sensor for detecting COVID-19 [9]. However, above all EDL platform devices are based on changes in electrical behavior and need a rigorous semiconductor fabrication process (plate capacitors, FET, etc.). Though the optical properties of EDL were discovered [10, 11]and their blueprint for light modulation was demonstrated, there are few reports on the optical device based on the optical properties change of EDL. Recently, in EDL, the giant Pockels effect of the water has been discovered [12], which is caused by the changes in the orientation of liquid molecules on the electrode surface.

Optic fiber phase shifters have attracted more and more attention due to their excellent compatibility, which can be directly used in current wavelength division multiplexing systems, fiber laser, and optical fiber sensors, without requiring alignment of fiber pigtail junction [13]. Compared with the silicon-based waveguides, the price of fibers is lower, and the device can be feasible [14, 15]. Among a range of outstanding fiber optic platforms, the microfiber platform is one of the spotlights due to its high sensitivity, miniaturization, and extremely high scalability. At present, a series of devices have been implemented based on the microfiber platform, such as microfiber sensors [16], microfiber coil resonator [17], and microfiber coupler [18]. Furthermore, the extension devices of microfibers also show good application prospects [19].

In this paper, to the best of our knowledge, we demonstrate a microfiber EDL platform based on the Pockels effect of liquid molecular for phase shifter. This prototype structure was constructed by integrating indium tin oxide (ITO) transparent electrodes on a microfiber platform [20, 21]. Immersion of this platform into liquid resulted in the formation of EDL at the interface of the ITO electrode and liquid. The effective refractive index (RI) in the EDL changed by modulating the orientation of liquid molecules by applying voltage. Subsequently, the transmission spectrum was modulated through the evanescent field of the microfiber. In our experiments, the fiber EDL platform has the advantages of low voltage modulation and simple fabrication.

The schematic diagram of the microfiber EDL phase shifter is shown in Fig. 1. The microfiber was produced by the fusion taper method through flame heating and drawing of single-mode fiber. The ITO transparent electrodes were sputtered by the radio frequency (RF) method on the microfiber, one electrode was completely covered in the sensitive region of the microfiber, and the other electrode was sputtered on the unstretched region. The magnesium fluoride (MgF_2) substrate was used to hold the liquid and not affect the interference spectrum of the transmission in the waveguide due to the lower refractive index of MgF_2. Due to the surface tension of the liquid, the aqueous solution can be supported on the surface of the MgF_2 substrate. In the configuration, the electric field was applied by connecting the two ITO electrodes to the power supply assisting with conductive silver glue.

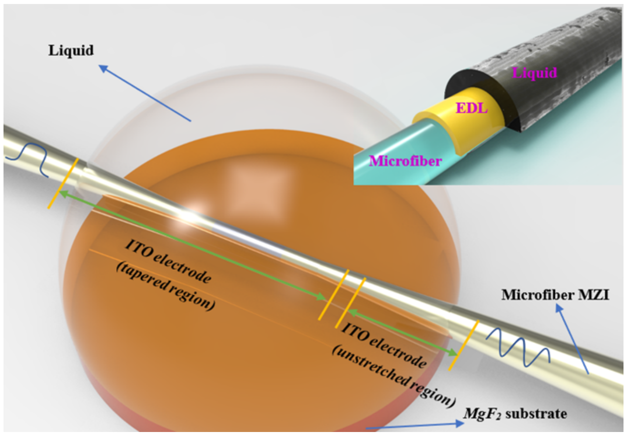

Fig. 1 The schematic diagram of the proposed microfiber EDL phase shifter, the inset: the diagram of the waist region.

The original interference spectrum of the non-adiabatic microfiber in the air is shown as the red curve in Fig. 2 (a), with the free spectral range (FSR) of 7.3 nm and the extinction ratio of 11.4 dB. By magnetron sputtering deposition system (JGP-450B), 35 nm ITO thin-film electrodes were sputtered on the upper surface tapered region of the microfiber and the unstretched region. The energy-dispersive X-ray spectroscopy (EDS) of the ITO thin film obtained by sputtering is shown in Fig. 2 (c). The illustration in Fig. 2 (c) shows the scanning electron microscope (SEM) image of the microfiber decorated with an ITO transparent electrode. The EDS comes from the SEM image. In the figure, In, Sn, O elements can be observed, which indicated that the ITO transparent electrode has been decorated on the microfiber.

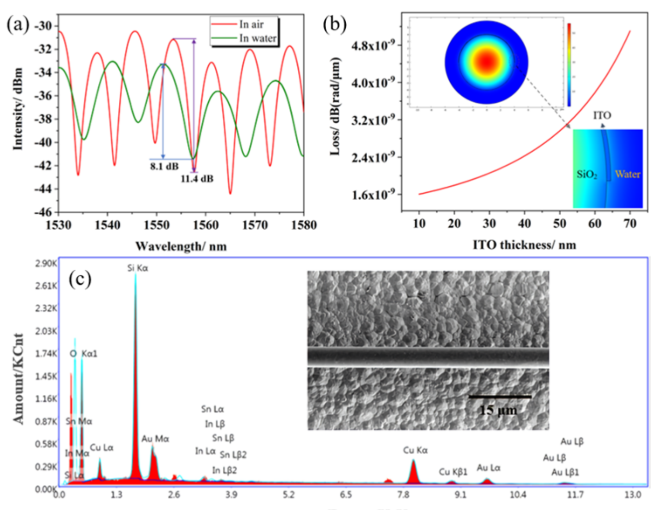

Fig. 2 (a) The interference spectrum of the microfiber in air and electrolyte. (b) The simulation loss result of the ITO transparent electrode coated on the microfiber. (c) The EDS of ITO, the inset: the SEM image of the microfiber decorated with ITO electrode.

The numerical simulation result shows the loss of the microfiber caused by ITO thickness changes and is shown in Fig. 2 (b). In the experiment, the adopted thickness of the ITO thin layer was about 35 nm. And the loss caused by the thin layer of ITO coverage is almost negligible monitored by the optical power meter. The interference spectrum in water is shown in the green curve of Fig. 2 (a). The extinction ratio of the interference spectrum in water was reduced to 8.1 dB, and the FSR broadens to 11 nm. The increase of FSR also increases the tunable wavelength range. The drop in contrast and light intensity is due to the difference in refractive index (~ 0.33) between an aqueous solution and air. Although the contrast is slightly reduced, a distinct interference envelope can still be observed.

In the experiment, the amplified spontaneous emission (ASE, 1520 nm-1610 nm) light was guided into the proposed microfiber phase shifter EDL platform, and monitored by an optical spectrum analyzer (OSA, YOKOGAWA AQ-6317B). To explore its phase-shifting characteristics, a series of gradient-increasing voltages were applied to the structure. The interference spectrums as a function of voltage were shown in Fig. 3. It can be found from the results that with increasing the voltage applied to the structure, the interference spectrum shifts to the long-wavelength direction. And as the voltage increases, the phase shift of the interference spectrum also increases regularly. With applying the maximum 1.4 V to the device, the maximum spectral shift was 3 nm. We attribute this phenomenon to the Pockels effect of the liquid. In the EDL between the electrode and the solution, when a voltage is applied, disordered water molecules are regularly arranged, and this molecular-level change causes a change in the refractive index. In our experiments, we found that the phase shift of the interference spectrum will not increase further by increasing the voltage. As the voltage increases, in the EDL, the water molecule orientation reaches equilibrium at a certain voltage, so that the effective refractive index of the EDL does not change and the phase of the interference spectrum will not be shifted. Meanwhile, to avoid the electrolysis of the water, a higher voltage was not suitable to be applied to the structure. This low-voltage phase shifter can be used in wearable sensing devices.

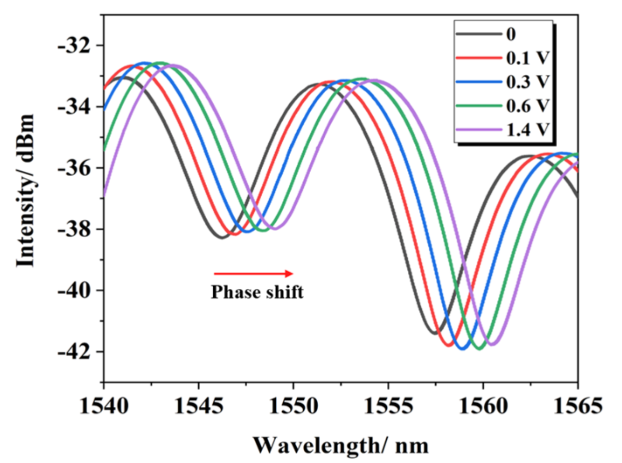

Fig. 3 The spectral shift of the proposed microfiber EDL platform response to voltage.

The fitting data of the spectrum shifts and the applied voltages are shown in Fig. 4. The fitted curve shows that the spectrum shows a non-linear shift, and it can be expressed as y=1549.28-2.95*exp(-

x/0.49). Although the spectral shift should be linear with the voltage based on the Pockels effect, in the experiment, the ITO electrode covered the upper surface of the microfiber. Therefore, the RI variation of the cross-section of the waveguide is not uniform, so the voltage and the phase shift show a nonlinear relationship. From the fitted data, the degree of change can be expressed as 6.02*exp(-x/0.49) nm/V. Here, we present two measures to improve this coefficient. This coefficient is expected to be improved by uniformly coating ITO transparent electrodes on the microfiber. The other is to reduce the size of the microfiber to improve the sensitivity. Please allow us to improve in follow-up work.

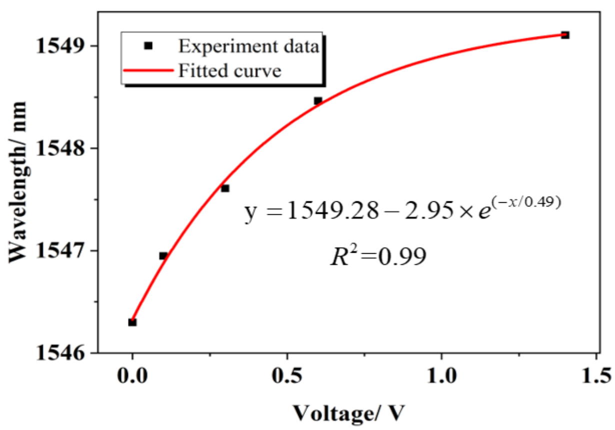

Fig. 4 The dependence of the wavelength shift with the application of voltages.

To investigate whether the spectrum shift was caused by the chemical reaction on the surface of the ITO-modified microfiber, the electrochemical process of the device was investigated. The 8 cyclic voltammetry (CV) measurements were detected in deionized water with the applying voltages of 0 V →-1.5 V →1.5 V →0 V and described in Fig. 5. It can be seen from the CV curves that there is no oxidation peak position and reduction peak position. The result confirms that almost no chemical reaction occurred on the surface of the ITO-modified fiber, that is, the spectrum shift wasn't caused by the chemical reaction [22].

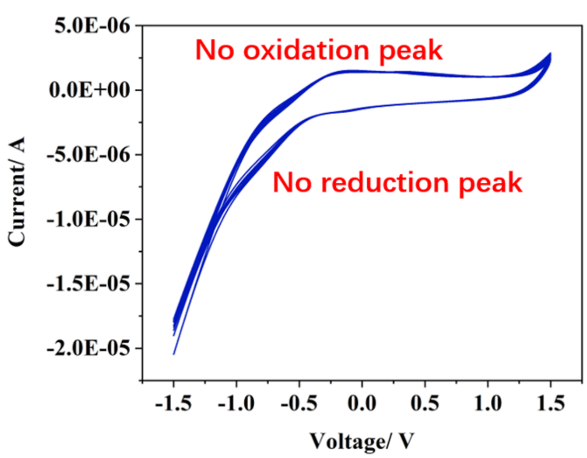

Fig. 5 The cyclic voltammetry curve of the ITO-modified fiber as the working electrode in the electrolyte.

To investigate the stability of the structure, here, we characterize the amount of phase shift as the change in light intensity at the corresponding wavelength. The signal light was guided into the monochromator (Zolix, Omni-λ300) and filtered into monochromatic light. The monochromatic signal light intensity was detected by an indium gallium arsenide detector (Zolix). In the experiment, the monochromator was set to only pass 1550 nm light. As shown in Fig. 6, by periodically applying a voltage, the corresponding light intensity also exhibits periodic changes, and the spectrum exhibits good stability in multiple cycles. It appears that this structure has good stability and recovery to the voltage response. The inset of Fig. 6 shows the response time of the structure. The rising edge and the falling edge time are about 1.5 s and 0.5 s, respectively. The rising and falling edge time may be due to the adsorption of ions on the electrode surface. And the substitution of ions for water molecules in EDL destroys the dipole layer of water molecules [23]. Unfortunately, we can not remove the electrolyzed hydrogen and hydroxide ions from aqueous solutions.

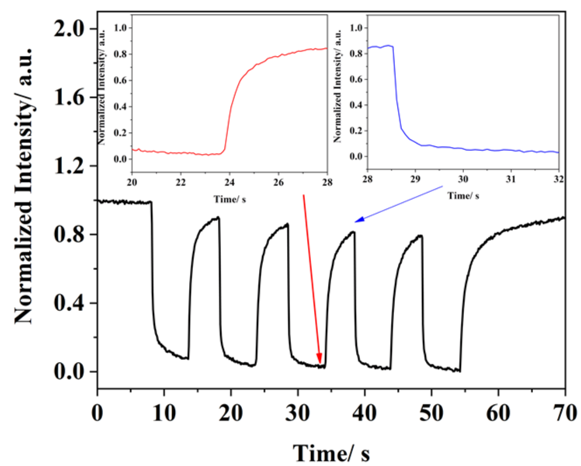

Fig. 6 The stability and the response time of the microfiber EDL platform.

The effect of charged particles in solution on the structure was investigated. In this experiment, NaCl aqueous solution was used as the experimental sample. Since the refractive index of NaCl solution has an obvious dependence on the concentration, the initial phase of the interference spectrum of the microfiber with different NaCl refractive indexes is also different. Therefore, the initial strength is different in Fig. 7. In the experiment, we mainly discuss the change value of the light intensity under the same voltage. Fig. 7 (a)-(c) shows the change of light intensity in 0 M, 0.1 M, and 0.3 M aqueous solutions under 0.5 V voltage application, respectively. We can see the intensity change gradually decreases with increasing concentration. According to the Debye Hückel length *d*, which can be used to estimate EDL thickness *d* [12]:

$$d = 0.304 M^{-1/2}$$

Here, *M* presents the concentration of the electrolyte aqueous solution. It can be known that an increase in concentration leads to a decrease in EDL thickness. Therefore, we attribute the decrease in the amount of concentration-induced phase shift to the decrease in the EDL layer. What's more, Agglomeration of charged particles may also cause a reduction in the refractive index change [24]. From the result, we can see that in different concentrations of electrolyte solutions, the device still has good stability. This should be attributed to the good chemical stability of ITO transparent electrodes [25].

To verify whether it is caused by the Pockels effect of water molecules, due to the absence of the Pockels effect in non-polar molecules, a non-polar molecule (cyclohexane) was used and the result is shown in Fig. 7 (d). The device did not exhibit the modulation function in cyclohexane. This result further confirms that the phase modulation is caused by the Pockels effect of the liquid in the EDL.

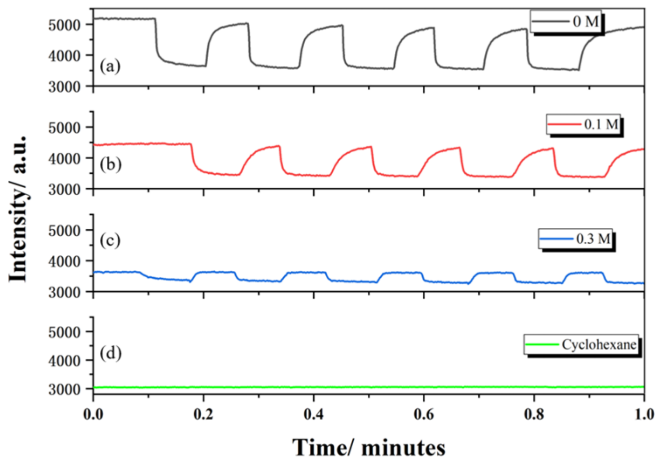

Fig. 7 The response of the device with different solutions.

In conclusion, we demonstrate a simple microfiber phase shifter based on the optical properties change in EDL. The ITO thin film transparent electrodes were integrated on the upper surface of a microfiber. The structure was submerged in the aqueous solution, and an EDL was formed at the interface of the ITO transparent electrodes and electrolyte. This microfiber EDL platform realizes an electro-optic modulation function by applying a voltage to modulate molecular orientation. The rising and falling edge times of the sensor are 1.5 s and 0.5 s, respectively. The integrated, scalable, and compatible microfiber EDL platform phase shifter has the potential for wearable sensing devices, biopotential detection, and biomolecule detection.

The authors declare no conflicts of interest.

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