ADVANCED OPTICAL MATERIALS

Supporting Information

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Electrospun Polymer Fiber Lasers for Applications in Vapor Sensing

Sarah Krämmer, Fabrice Laye, Felix Friedrich, Christoph Vannahme, Cameron L. C. Smith, Ana C. Mendes, Ioannis S. Chronakis, Joerg Lahann, Anders Kristensen, and Heinz Kalt**

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Measurements of the Lasing Threshold

In order to determine the lasing threshold of the fibers the sample was pumped with increasing pump fluence and spectra were acquired. As soon as the lasing threshold is overcome sharp lasing peaks on top of the fluorescence background can be observed. The integrated intensity of the lasing peak which arises first is then plotted versus the pump fluence (see Figure S1). Above lasing threshold an increase in slope is observed and the threshold is determined from the intersection of the two lines fitted to the data points below and above threshold.

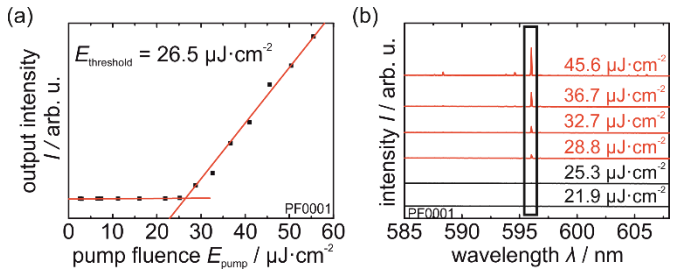

Figure S1: Typical measurement of the lasing threshold. (a) So-called input-output curve showing the integrated intensity of the lasing peak versus the pump fluence. The threshold is determined as the intersection of the two lines fitted to the data points. (b) Spectra for varying pump fluences clearing showing the arising sharp lasing modes when the threshold is overcome.

As mentioned in the main part the resonators in the fiber networks are formed randomly during the fabrication process. This means that each resonator is individual and hence also exhibits a different lasing threshold due to distinct quality factors.[19] For the sensing experiments cavities with low lasing thresholds were chosen to reduce the required pump fluence and bleaching effects.

Anisotropic Expansion of Electrospun Fibers

The macromolecules in electrospun fibers can be aligned along the fiber longitudinal axis. Therefore, it is possible that the expansion of the fibers when exposed to alcohol is not isotropic and radial changes are more likely to occur. Since it is beyond the scope of this work how exactly the fiber expansion occurs, in the publication we assumed isotropic expansion which is the simplest case. However, within the supporting information we also want to present how anisotropic radial expansion of the fibers affects the shift of the lasing modes. In the following we will consider the extreme case where the complete increase in film thickness is transferred to an increase in fiber radius and there is no change in fiber length. We obtain the following equation for the relation of the film volume to the fiber volume:

$$\alpha V = V + \Delta V = \pi \cdot L \cdot (\gamma R)^2 = \gamma^2 V. \quad (1)$$

The wavelength shift can then be written as:

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta n_{\text{eff}}}{n_{\text{eff}}} = \frac{\Delta n_{\text{eff}}(\Delta R) + \Delta n_{\text{eff}}(\Delta n_{\text{PMMA}})}{n_{\text{eff}}}. \quad (2)$$

Figure S2 depicts the resulting wavelength shift for ethanol and methanol when only radial expansion is assumed for different concentrations. The change of the refractive index of the PMMA is the main contribution to the wavelength shift and the contribution due to radius changes is negligible. Since changes in radius only weakly contribute to a wavelength shift also the sensitivity is lower when only radial expansion is assumed compared to isotropic expansion. As we observed higher sensitivities in the experiment we assume that also a change in fiber length occurs and contributes to the wavelength shift.

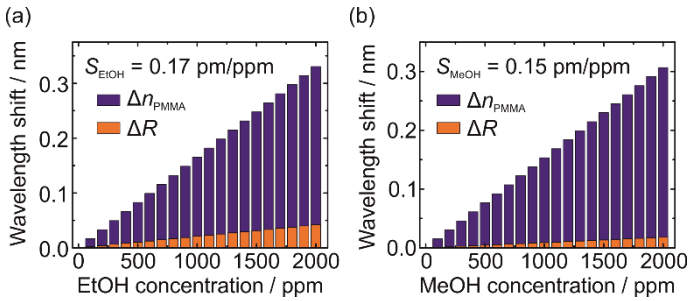

Figure S2: Expected shifts of the lasing modes when the fibers are exposed to (a) ethanol or (b) methanol vapor and when bare radial expansion of the fibers is assumed. The total shift is

split into contributions from refractive index changes of PMMA ($\boldsymbol{\Delta n_{PMMA}}$), and changes of the fiber radius ($\boldsymbol{\Delta R}$).

Modified Data Analysis

In order to shorten the measurement duration, data analysis can be modified when the analyte and its saturation time are known. The shift in saturation A, which gives information on the analyte concentration, can be determined from the slope of the saturation curve at $t = 0$ s:

$$\frac{d\,\Delta\lambda(t)}{dt} = \frac{A}{\tau}\exp(-t/\tau) \quad \overset{t=0}{\longrightarrow} \quad \frac{A}{\tau}. \tag{S1}$$

By fitting a line to the first data points and by using the characteristic saturation time for the analyte-fiber combination τ the shift in saturation A can be determined.

In the following, we show that this analysis can be applied to the data obtained for ethanol. By doing so, measurement durations of 300 s, corresponding to 12.5 % of the saturation time, are sufficient to determine the ethanol concentration. **Figure S3**(a) depicts an example of a linear fit to the first data points. Since manual valves were used to adjust the ethanol concentration a short time is needed until stable flow is reached, which is why we neglected the first two data points for analysis. We performed the described fitting procedure for all measurements and used the average saturation time of $\tau = 2400$ s determined previously to calculate the shift in saturation A. In Figure S3(b) the wavelength shift in saturation is plotted over the ethanol concentration. For low concentrations a linear behavior is observed and a sensitivity of $S = 0.98$ pm/ppm is obtained from the slope of the fitted line. When comparing the results obtained with this method with the results where the complete data was represented by an exponential fit function one finds good agreement. Hence, the presented analysis is a promising method to abbreviate the measurement duration when the analyte and its saturation time are known.

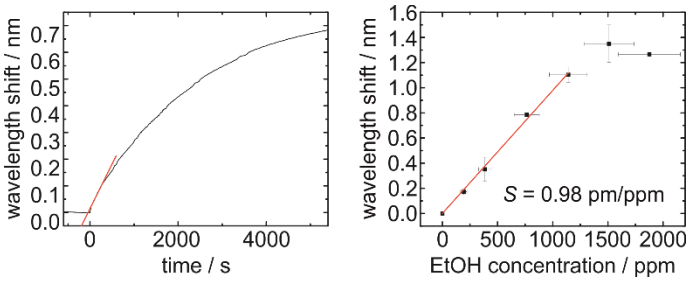

Figure S3. (a) Example of a linear fit to the data points obtained during the first 300 s of the experiment. (b) Shift in saturation determined from the slope at t=0 of the data for different ethanol concentrations. For low concentrations a linear behavior is observed. The sensitivity, which is determined from the slope, agrees well with the sensitivity obtained when the complete data is evaluated.