

Dye-doped optical sensor for the detection of biodiesel in diesel

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Materials and Methods

All solvents were purchased from Fischer Scientific and used as received. Ethyl cellulose (49% ethoxy content) was purchased from MP Biomedicals and Nile Blue chloride (NBC, 85%) was purchased from Sigma-Aldrich. Methyl hexanoate (98%) was purchased from Eastman, and methyl myristate (>98%) methyl oleate (>96%) methyl behenate (>90%) were purchased from Fischer Scientific and used as received. These FAMES were used for make standard solutions in kerosene. Biodiesel (B20) containing 20% v/v FAME was purchased from a Pilot gas station in Knoxville, Tennessee.

Sensor Fabrication and Analyte Exposure

Standard microscope slides (Corning) were cut to 1 cm² squares and used as the sensor substrate. The glass squares were washed in a piranha solution (concentrated H₂SO₄ and 30% H₂O₂ in 3:1 ratio) for 30 min, followed by washes with acetone, methanol, ethanol, rinsed with deionized water, and allowed to dry in the oven before use. N-type [100] silicon wafers were similarly cleaned for deposition of thin film sensors that were then used for characterization by SEM.

Ethyl cellulose (~0.750 g) was dissolved in a 1:1 mixture of toluene and ethanol and sonicated for approximately 4 hours to ensure that the ethyl cellulose was completely dissolved in solution. The result was a viscous ethyl cellulose solution (7.5% wt EC). NBC (~1 mg) and methanol (350 μ L) were added to 1.10 g of ethyl cellulose solution with stirring. This mixture was allowed to stand and cure for several days in a capped vial prior to use. After curing, the mixture was pipetted onto a clean glass slide and drawn to the edges of the glass with a plastic pipette tip. The slide was then spun at ~2600 rpm for approximately 1 min in a custom built spin-coater. After spin-coating, a freshly made thin film sensors with a distinct blue color were placed in a Schlenk tube and pumped at 0.01 mmHg vacuum for 1 hour. They were then stored prior to use.

The FAME mixture was made by combining methyl hexanoate, methyl myristate, methyl oleate, and methyl behenate in an evenly distributed 1:1:1:1 ratio. This mixture provides methyl esters with varying chain lengths (C6–C23) with methyl oleate offering a CH=CH bond in its chain. Different concentrations of the FAME mixture were made by diluting the mixture to the appropriate concentration with diesel. Sensors were submerged into their respective vials containing 20.0 mL of varying diesel/FAME concentrations while the solution was stirring. After satisfactory analysis time, the sensors were taken out of their vials and analysed using a UV-Vis spectrometer.

The sensor response to 20.0 mL of FAME, ranging from 0.500–30.0 ppm, is less than 30 min. To achieve this response time, two steps have been taken to allow faster diffusion of FAME into the sensor film and reduce the response time. First, the mixture of ethyl cellulose and NBC dye needs to be spin-coated at 2600 rpm (revolutions per minute) to make a thin sensor film. Second, the freshly-made sensor film is subjected to a dynamic vacuum (<0.01 mmHg) for

1 hour to remove toluene and excess MeOH/EtOH in the film. After the vacuum treatment, the sensor remains blue, indicating that there is sufficient MeOH/EtOH around the NBC dye molecules in the sensor. These steps reduced the response time from originally over 1 h (without the vacuum treatment) to <30 min.

Instrumentation

An Agilent 8453 UV-Vis spectrometer using two light sources, a deuterium and tungsten lamp, was used to acquire absorbance spectra of the sensing films. A quartz cuvette with a 1 mm pathlength was utilised to hold the sensor in place. Spectra were recorded in the range from 190 cm^{-1} to 1100 cm^{-1} . Peak deconvolution and baseline correction were achieved through Origin software. SEM images of the sensors before and after exposure to FAME were taken using a Leo 1525 Field Emission Scanning Electron Microscope.

Scanning electron microscopy (SEM) imaging was taken in order to characterise the surface of the FAME sensor before and after exposure to the FAME mixture. The images show “porous pitting” features consistent with the phase separation that occurs during the processing of the sensor with no discernible difference on the surface of the sensor before or after exposure (Supporting Fig. 3). The porosity and polar features of the cellulose film allow FAME to preconcentrate and diffuse into the sensor, causing a color change.

Stability Tests

Experiments were performed to test the stability of the FAME sensor over different periods of time. Extra sensors not used in previous experiments were kept in open air and then tested four months later against FAME sensors made a week ago and freshly made sensors made

one day ago. These sensors were each exposed to real world samples of 1% biodiesel and examined in the UV-Vis. A side by side comparison in Table 1 shows that a freshly made sensor and a week old sensor have only a 0.3% error in absorbance at 502 nm while a sensor made 4 months ago left in open air had a 3% difference when compared to the freshly made sensor. This demonstrates that a sensor made several months ago is able to perform similarly to a freshly made FAME sensor that was fabricated only a day ago.

Additional Biodiesel Studies

The FAME mixture used in previous experiments consisted of 4 different kinds of FAME ranging from C6 – C23 which was used as a mimic for biodiesel standards. However, the FAME mixture that was used as standards is not entirely representative of the FAME composition found in biodiesel in the U.S and Europe, where methyl esters C16 and C18 dominate. Further tests have been performed using our FAME sensor on real world biodiesel samples (containing C16 or C18 fatty acids with unsaturation sites) over the range of 100 ppm–20.0% FAME instead of a FAME mixture to serve as methyl ester standards. The data was analyzed using UV-Vis spectrometry and modelled using a logarithmic curve function (Supplementary Fig. 5). The data is similar to previous experiments using FAME standards where the sensor undergoes a saturation effect. The absorbance (A) vs. $\ln(x - x_0)$ of the biodiesel data gives a linear line with $R^2 = 0.993$ (Supplementary Fig. 5). These studies using biodiesel give a better representation of the target analyte and the detection of FAME. This study along with previous studies shows that this FAME sensor can detect FAME at a full range from 1.00 ppm to 20.0%.

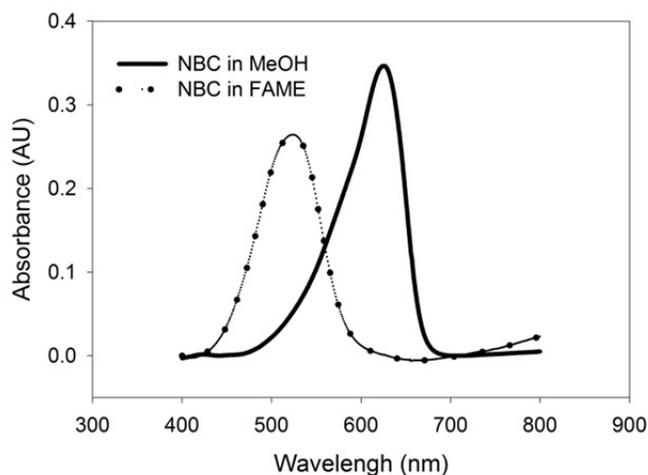


Fig. S1 The absorbance of NBC when dissolved in MeOH (625 nm) and FAME (525 nm).

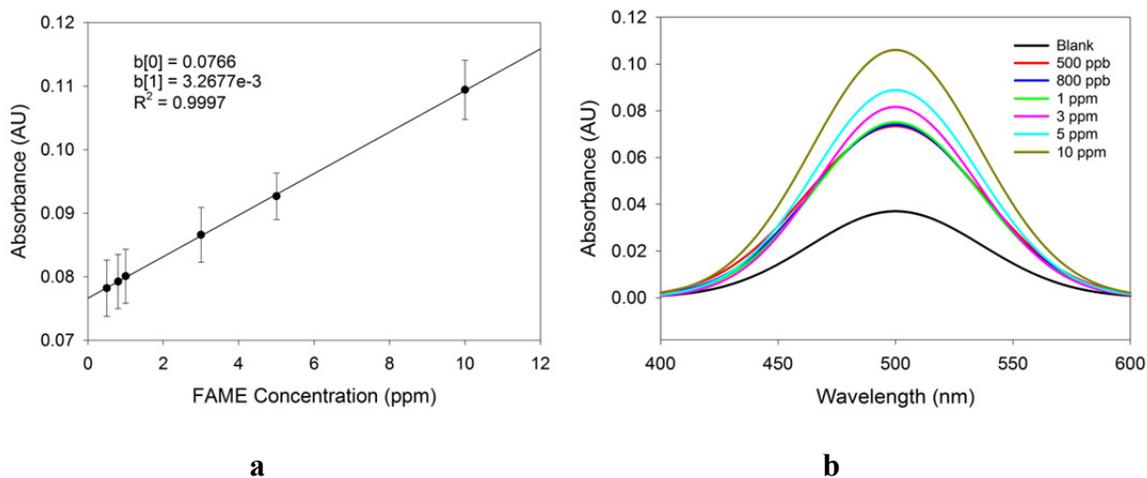


Fig. S2 (a) Calibration plot of the sensor demonstrating the detection of FAME from 0–10.0 ppm. (b) Absorbance spectra showing the peak at 500 nm increasing with increasing concentrations of FAME mixture.

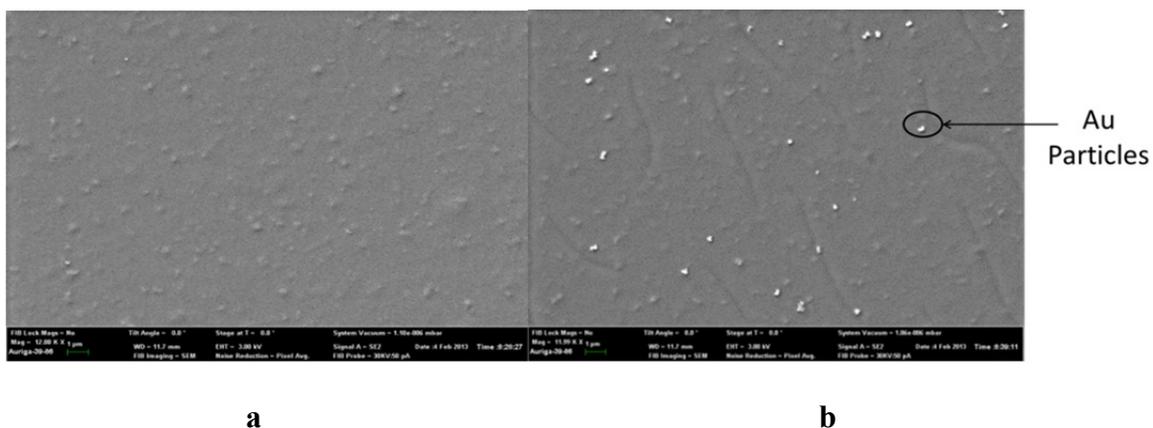


Fig. S3 SEM surface images of the thin film sensors before (a) and after (b) exposure to FAME. The white particles in Fig. 2b are due to the sputtered gold particles needed on the sensor's surface to increase the conductivity for SEM imaging.

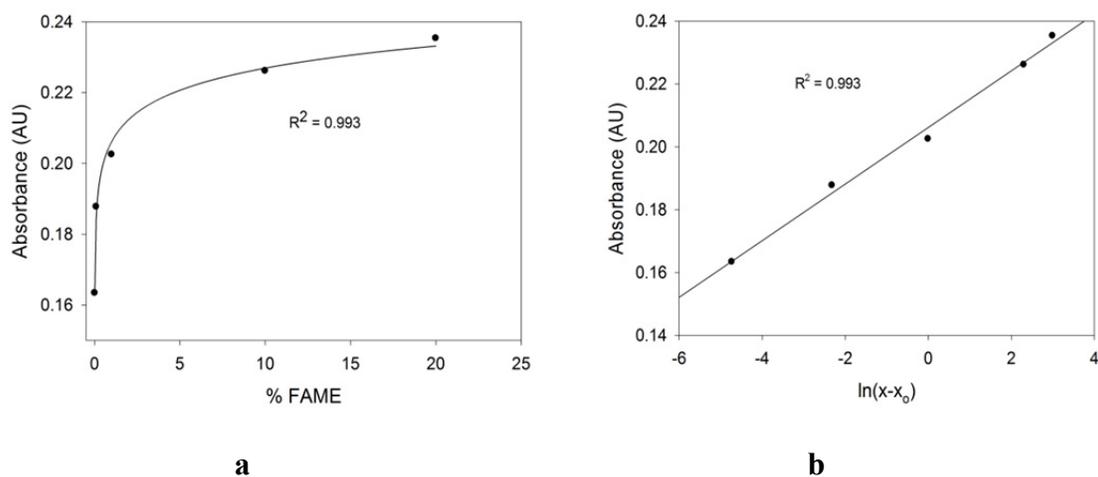


Fig. S4 (a) Detection of 100 ppm–20.0% v/v biodiesel modeled by a logarithmic curve function
(b) Data plotted as a function of absorbance (A) vs. $\ln(x - x_0)$.

Table S1. Comparison of the tests of three sensors

	Fresh sensor	1-week-old sensor	4-month-old sensor
Absorbance at 502 nm (AU)	0.1622	0.1617	0.1577

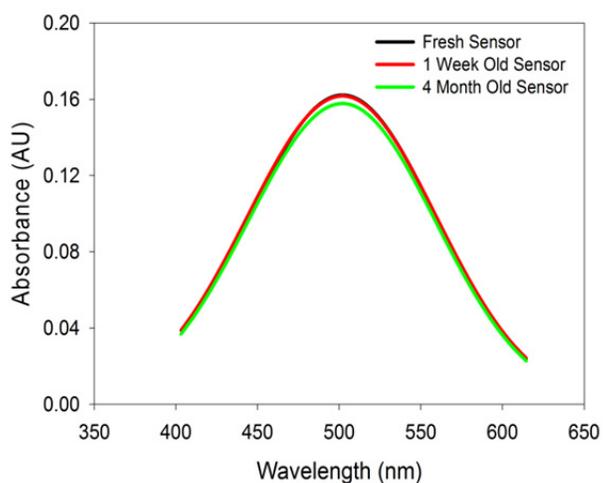


Fig. S5 Comparison spectra of FAME sensors when fresh, a week old, and 4 months old exposed to 1.00% biodiesel.