Single-walled carbon nanotubes coated D-shaped fiber for aqueous ethanol detection*

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In this letter, single-walled carbon nanotubes (SWCNT) coating was used on the D-shaped silica fiber for ethanol sensing in aqueous solution. The performance of this structure as an ethanol sensor was studied here by monitoring output power variation and wavelength shift with changing ethanol concentration. In the concentration range of 5%—50% of ethanol, the SWCNT coated structure showed an improved sensitivity compared to the uncoated sample. The sensitivity is improved from 0.013 5 dB/% to 0.040 9 dB/% with the coating. The SWCNT coated sample also showed a peak wavelength shift of 0.1 nm with the change of ethanol concentration in the same range.
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Ethanol is widely used in industrial and medical applications. It is also important in bio-fuel processing[1]. However, ethanol is a highly volatile, corrosive, and flammable material, limiting the performance of traditional sensors that depend on resistors and voltage changes[2,3]. Additionally, traditional ethanol detection methods, such as mass spectrometry and high-pressure liquid chromatography, currently called high performance liquid chromatography, require complex operations, larger test samples, and professionally trained operators[4]. Since ethanol is essential for many foods, electronics, biomedical and chemical industries, detecting ethanol in aqueous solutions is vital for the safety and quality of these industries[5].

Fiber optics sensors can provide solutions to the challenges faced by traditional ethanol sensors due to their immunity to electromagnetic interference, ability to function in a wide range of temperature, and large bandwidth[6,7]. Fiber sensors have been used to detect uric acid, formaldehyde, methanol, and many other chemical analytes[8-10]. Fiber sensors can be built using various sensing structures, such as tapered fiber[8], micro-loop resonator[9], and micro-bottle resonator[11]. D-shaped fiber structure is one of the choices because of its advantageous of ease of construction, convenience of coating due to their large surface and mechanical stability[12].

Single-walled carbon nanotubes (SWCNT) coatings have attracted a lot of attention in chemical detection applications due to their large surface area, chemical stability, and excellent biocompatibility[13]. Additionally, SWCNT materials have excellent optoelectrical properties and good mechanical stability[14]. SWCNT materials have a large surface area to volume ratio. Greater surface area enhanced interactions between the analyte and the sensing structure, resulting in improved sensitivity[15]. Thus, using SWCNT coating on fiber optics sensors is a promising choice.

In previous work, tapered multimode plastic fiber was used to detect ethanol and showed a sensitivity of 1.527 mV/%[16]. There have been many attempts to make fiber ethanol sensor and many of them used multimode fiber. For sensing application, multimode fiber was coated with various elements such as graphene oxide[17], silver nanoparticle-incorporated reduced graphene oxide (Ag/rGO)[4], carbon nanotubes (CNT)[15] and conducting polymer[18] were also studied as ethanol sensors with multimode fiber. In this work, we used SWCNT as a sensitive coating and D-shaped silica single mode fiber as a sensing structure to detect ethanol concentration in aqueous solutions.

A silica single mode fiber cable (Corning-28) was side-polished to obtain the sensing structure. 1 cm of the fiber was stripped of buffering and cleaned with alcohol. Then, the fiber was side-polished using sandpaper rotation by a 5 V direct-current (DC) motor until the diameter

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of the D-shaped reached 84 μm during polishing. The light from an amplified spontaneous emission (ASE) light source was launched into the fiber and the output power was continuously monitored by an optical power meter (OPM, ThorLab PMD100). This D-shaped diameter is ideal because it is small enough to increase the light interaction with the surroundings with as little fragility as possible. The polishing causes the output power of the sample to drop by 3 dB.

To prepare the SWCNT coating, 250 mL of deionized water was mixed with 2.5 mg sodium lauryl sulfate. This solution was stirred for 1 h. Then, we took 45 mL of that solution and added 5 mg SWCNT. This mixture was stirred for 24 h and then sonicated for 72 h. For coating the D-shaped fiber, 2 mL of the SWCNT mixture and 2 mL of polyvinyl alcohol (PVA) solution were mixed and applied to the fiber. The coating was applied three times and left to dry for 24 h after each layer application before the experiment. Fig.1 shows the prepared D-shaped silica fiber coated with SWCNT coating. As shown in the figure, the SWCNTs were homogeneously coated on the fiber surface. It has a diameter of about 84 μm. It also should be mentioned that the SWCNT coated D-shape fiber has an optical loss of about 3.2 dB at 1 550 nm.

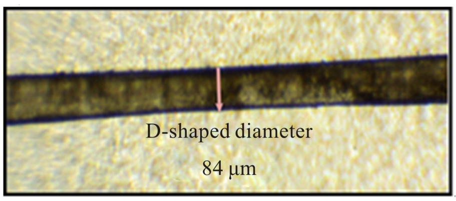

Fig.1 D-shaped silica fiber sample coated with SWCNTs

In Fig.2, two experimental setups are shown for ethanol sensor measurement. First, the shaped fiber is connected on one end to a tunable laser source (TLS, ANDQ 4321) and connected to an optical power meter (OPM, ThorLab PMD100) on the other end as shown in Fig.2(a). The D-shaped region is put in a dish with the ethanol solution. This setup was used to track the sensor's output power response to ethanol concentration variations. In this experiment, the D-shaped fiber sample was put carefully into a Petri dish with the ethanol solutions. After each step, the solution was discarded, the sample was washed gently with deionized water and left to dry. The same sample was used for both experiments with uncoated and SWCNT coated sensors. The wavelength used throughout the experiment was 1 550 nm. The temperature was kept at a constant value of 25 °C. The focus of this sensor will be to detect ethanol and in future work more liquid solutions will be used to test the sensor with various coatings.

The setup used to monitor the wavelength shift of the sensor is shown in Fig.2(b). The fiber connected to the TLS is maintained while the other fiber end is connected to an optical spectrum analyzer (OSA). This setup helps in tracking the shift of the sensor spectral output with the changing ethanol concentration.

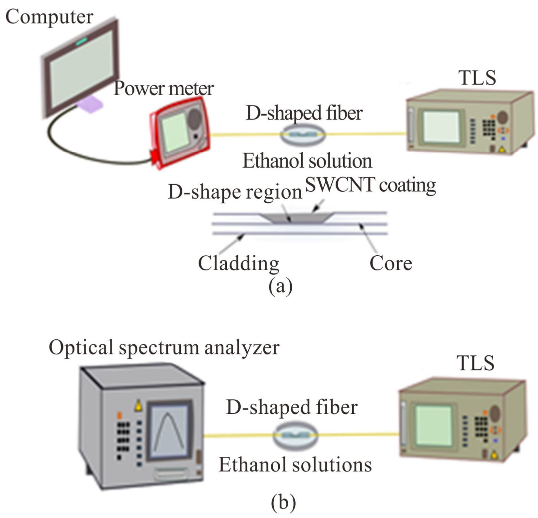

Fig.2 Experimental setup for the ethanol sensor based on (a) power variation and (b) wavelength shift measurement

Fig.3 shows the change in output power with the variation of concentration of ethanol aqueous solution. Before applying the SWCNT coating layers, the output power of the structure drops from −0.4 dBm to −1 dBm as the ethanol concentration increases from 5% to 50%. For the SWCNT coated sample, the output power drops from −1.5 dBm to −3 dBm in the same range of ethanol concentrations.

In previous work, it has been shown that the refractive index of ethanol increases from 1.335 to 1.350 as the ethanol concentration increases from 0 to 50%[18]. The analyte (ethanol) absorption into the sensing coating (SWCNT) results in the changing refractive index of the coating and affecting the propagation characteristics of the entire sensing structure. The increase in the cladding refractive index caused by the ethanol increasing concentration causes this drop in the output power. This refractive index increase lowers the contrast in the refractive index between the cladding and the core, causing more light to escape and greater losses.

The SWCNT coating improves the sensitivity of the sensing structure due to the polar COOH groups on the CNT surface, these groups response to ethanol, and the resulting dipole-dipole interaction between the COOH groups on the CNT and the polar organic ethanol molecules. Thus, the -COOH group of the coating and OH groups of the analyte become attached, causing interactions through hydrogen bonds and changes to the sensor light output. Consequently, the O-H stretch of water molecules becomes smaller due to the carbon molecules' presence in ethanol solutions[16]. This shows how SWCNT improves the sensing structure response to ethanol solutions.

Fig.3 also indicates that the SWCNT coated sample has an improved sensitivity of 0.040 9 dBm/% compared to the uncoated sensitivity of only 0.013 5 dBm/%. The linearity of the coated sample was 98%. On the other hand, the uncoated sample had 94% linearity. Fig.4 also shows the performance of the sensor in three connective runs. It indicates that the power variation is smaller with the coating of SWCNT.

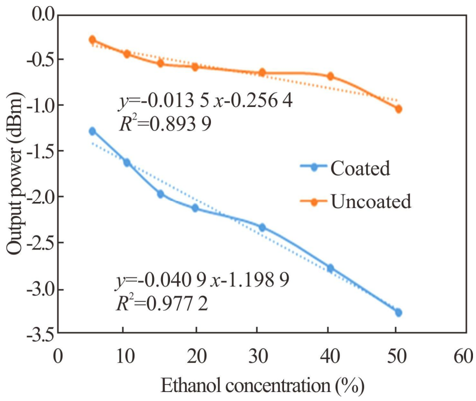

Fig.3 Transmitted power of the sensor as a function of ethanol solution concentration

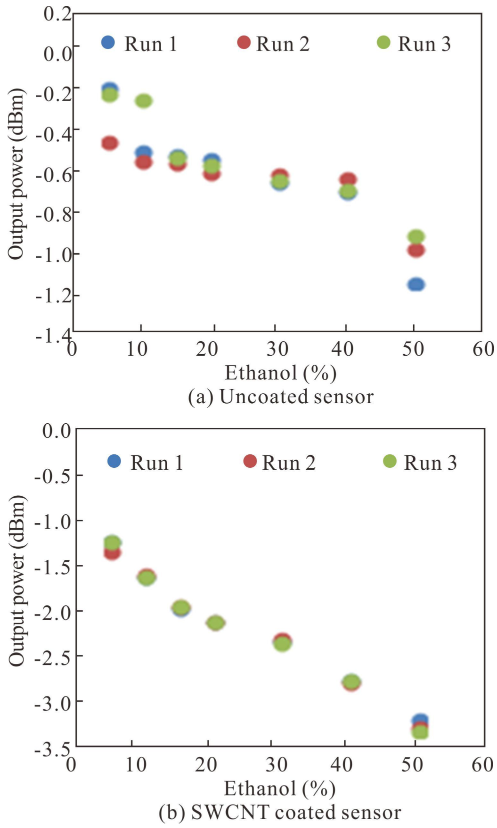

Fig.4 Outputs of (a) uncoated and (b) SWCNT coated sensors in three different runs, respectively

The stability of the proposed SWCNT sensor is presented in Fig.5. The output power of the sensor was continuously measured and recorded for 300 s. The coated sample shows little variation with time. The stability of the sensor is improved with coating due to the interaction between the carbon nano tubes and the ethanol.

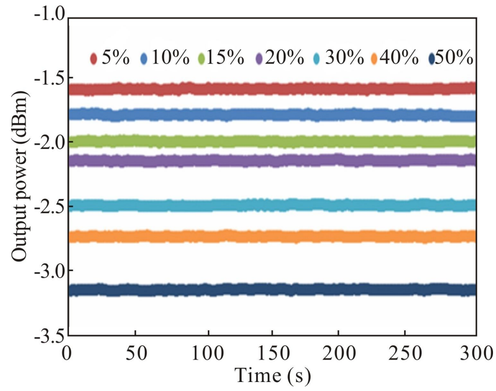

Fig.5 Stability of the proposed sensor

Fig.6 shows the SWCNT transmission spectra at different concentrations of ethanol solutions. The peak wavelength shifted from 1 549.72 nm to 1 549.81 nm as the ethanol concentration in the tested solution increased from 5% to 50%. This shift is due to the increased refractive index of the ethanol solution. The uncoated sample did not show a repeatable wavelength shift during this experiment. Some of the curves are varied and saturated due to the small changes in refractive index. A further optimization in the sensor probe is required to detect a small increment in ethanol concentration.

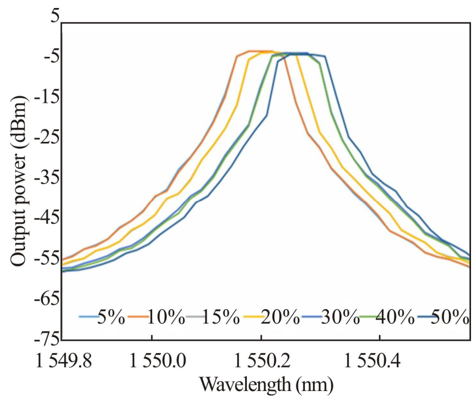

Fig.6 Transmission spectra of the proposed sensor

The stability of this sensor within the temperature range of 24—36 °C was investigated and the results are shown in Fig.7. The output power of the sensor did not have large variations in that temperature range. This is due to the good stability of the coating and the D-shaped sensing structure in a normal range of temperature.

A summary of the sensing parameters of the proposed sensor is presented in Tab.1. Applying an SWCNT coating improves the ability of D-shaped fiber to respond to changes in ethanol concentration. The sensitivity of the coated fiber was 0.040 9 dBm/% compared to that of the uncoated sample which was 0.013 5 dBm/% only. The coating also improved the resolution and linearity of the sensor.

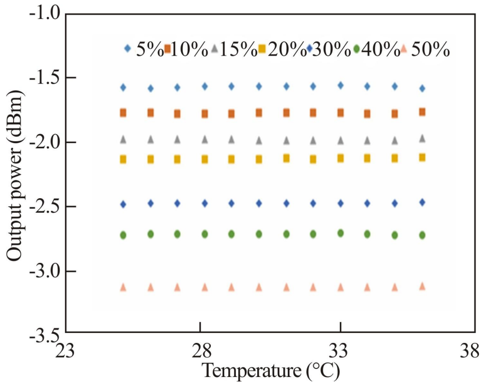

Fig.7 Output power at various temperatures

Tab.1 Sensing parameters of the sensors

Parameters	Uncoated sensor	SWCNT coated sensor
Sensitivity (dB/%)	0.013 5	0.040 9
Average standard deviation (dBm)	0.078	0.027
Resolution (%)	6.669	0.820
Linearity (%)	94.546	98.853

In conclusion, an optical sensor using D-shaped silica fiber coated with SWCNT for ethanol detection in aqueous solutions was developed here. The coated D-shaped sample showed an improved sensitivity over the uncoated D-shaped sample. The linearity and resolution of the coated sample were also improved after coating. In the future work, we will explore this design's ability to detect ethanol in gas form.

Statements and Declarations

The authors declare that there are no conflicts of interest related to this article.

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