Design of a smartphone plastic optical fiber chemical sensor for hydrogen sulfide detection

Smartphone plastic optical fiber chemical sensor for hydrogen sulfide (H_2S) detection

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We present a low-cost chemical plastic optical fiber (POF) sensor based on a smartphone hydrogen sulfide (H_2S) detection. The sensor uses smartphone flashlight as source and camera as pixel-based intensity detector. The POF is interconnected to the smartphone with a 3D-printed connector on both source/detector sides. A mobile application handles data acquisition on Android operative system. The sensor is functionalized to remote H_2S detection through silver deposition on the POF outer surface. Experiments demonstrate the feasibility of the sensor system as the presence of H_2S is successfully measured through an increase of optical losses through the POF link. This cost-effective, scalable, and compact sensor is promising for application in environmental sensing.

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The advent of smartphones has provided ubiquitous pocket devices available to billions of users worldwide. Recently, several research outcomes showed the possibility to use smartphones for optical sensing, exploiting its broadband flashlight as light source, its camera detector, or both, as building blocks of the system [1-5]. Several works have shown the possibility to perform biological and biochemical detection through externally mounted devices, using the smartphone as a platform for surface plasmon resonance detection [1-2], immunosensors [2, 5], chemical analysis of water constituents [3-4], or spectroscopy [3]. These architectures are designed for sensing, spectroscopy, or imaging on smartphone, ultimately aiming at replacing bulky instrumentation with pocket devices.

However, in environmental sensing applications, it is often required to perform remote detection, particularly for detection of deadly gases. This feature can be enabled through the use of fiber optic sensors (FOS), which have low optical attenuation, immunity to electromagnetic fields, and are fire-safe and chemically inert. Plastic optical fibers (POF) in particular have a high numerical aperture (NA), which facilitates light coupling. A first demonstration of smartphone-fiber sensing unit was performed by Bremer and Roth [1], requiring however the use of an external diffraction grating that complicates the device.

In this Letter, we propose a fully smartphone-POF sensing unit for chemical sensing of hydrogen dioxide (H_2S). Hydrogen sulfide is a highly toxic, inflammable and corrosive gas. Petro–chemical industries, coal mines and sewage treatment plants are the main sources of H_2S. Human body is vulnerable to H_2S through the respiration and nervous system. It causes blood poisoning and continuous exposure to concentrations between 10 and 550 ppm lead to the damage of internal organs and serious respiratory conditions and at higher concentrations can result in lethal outcome [6]; H_2S is listed as one of the main causes of death in the petrochemical industry. In order to detect the exposure to H_2S in real-time, with a rapid-response, and through ubiquitous device, overcoming chromatography and atmospheric sensing, we propose to integrate the sensing element on a silver-coated POF fiber [7], and interconnect it to a smartphone. In a practical application, this architecture allows placing the sensing element remotely with respect to handheld smartphone, and therefore can perform gas detection avoiding human exposure.

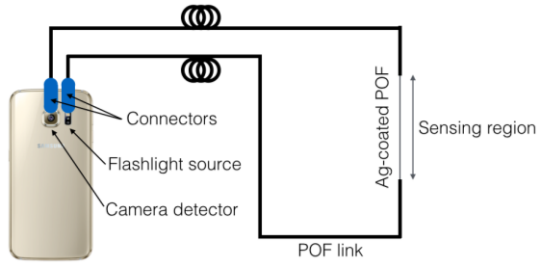

Fig. 1. Concept of the smartphone-POF system.

The concept of the system is illustrated in Fig. 1. The whole sensing architecture is constituted by three main parts: the smartphone is used as both light source (flashlight) and pixel-based intensity detector (camera); a 3D-printed connector is used to interconnect both source and detector to the POF used for the fiber link; the sensing element is a silver-coated POF, whereas exposure to H_2S induces an increment of optical losses through the sensing length. The use of a 3D-printed inexpensive connector makes the system scalable and easily adaptable to commercially available smartphones. Unlike previously reported works [2-5], the proposed system is instead all-smartphone-fiber, which is a key advantage in chemical sensing, because we can combine the remote sensing capability offered by optical fibers with the possibility to use a pocket ubiquitous device for detection.

The fiber used in this design is a POF made of polymethyl methacrylate (PMMA) having 0.98 mm core diameter surrounded by 0.01 mm fluorinated cladding, with NA 0.47. For the development of the sensing component, Tollen's reagent method was utilized to cast the POF with silver [7], as shown in Fig. 2. Fluorinated cladding was first removed immersing the fiber for 40 seconds into ethyl-acetate. After the cladding has been stripped off, the fiber was rinsed in 0.4 ml of tin chloride dehydrate solution. The POF was sensitized by submerging it into a 50 ml water-based solution consisting of 2.5 g of tin chloride ($SnCl_2$) and 3 ml of hydrochloric acid (HCl) for 15 minutes, as shown in Fig. 2(a). Afterwards, Tollen's reagent was prepared by mixing equal parts of a water-based solution of 0.10 M $AgNO_3$ and 10% of 15 M NH_3 with a water-based solution of 1.5 μM Rochelle salt ($KNaC_4H_4O_6$) and 0.25 μM magnesium sulfate ($MgSO_4$). 4 ml from each of these solutions were mixed together and diluted with 56 ml of water. This final step towards functionalization is shown in Fig. 2(b). To ensure a solid adhesion, the reaction was performed in a dark room and for duration of 1 hour, which showed to be a good trade-off between strength of adhesion and sensitivity to H_2S. Fig. 2(c) shows two Ag-coated POF sensors fabricated with this method.

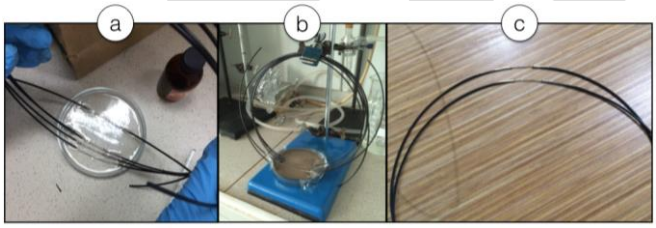

Fig. 2. Photographs of the Ag-coating POF functionalization. (a) After fiber stripping, POFs are submerged in a water-based solution; (b) deposition of Tollen's reagent on the POFs; (c) finalized sensors.

The principle of operation is based on the detection of the intensity changes of the light propagating in a silver-coated POF fiber when the gas is present the sensing region. The reaction underlying the intensity change involves the sulfide and Ag coating: $2Ag^+ + S^{--} \rightarrow Ag_2S + 2e^-$ [8]. Silver sulfide (Ag_2S) is a product of this reaction, and decreases the brilliance (i.e. reflectivity) of silver coatings, which leads to the lower light intensity transmitted through the sensing region.

The smartphone used for experiments is a Samsung Galaxy S6 Edge model, with Android operative system. The smartphone has dimensions of 142.1 × 70.1 × 7 mm and 16 MP rear camera equipped with autofocus and LED flash. In order to have a qualitative measure of flashlight beam divergence, we measured the half-angle beam divergence of the flashlight as ~47°.

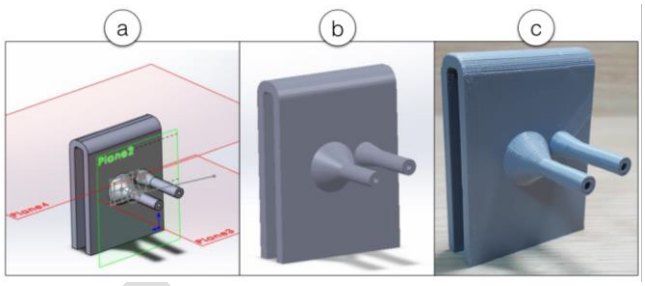

Fig. 3. 3D-printed connector that handles the flashlight-POF and POF-camera connections. (a) Solidworks® CAD model; (b) stereolitographic model; (c) photograph of the fabricated connector.

To facilitate the light coupling from the flashlight LED to the POF and from the POF to the camera, protect the fiber ends from environment and stray light, and ensure a stable alignment between fibers and source/detector, we developed a custom-made connector with a 3D printer. At first, we designed the connector CAD (computer-aided design) model in SolidWorks®, as shown in Fig. 3(a-b). This design ensures a relatively strong coupling of light from both source and detector side: this choice allows us to saturate the light intensity in the brightest pixels, while obtaining an intensity close to zero in the background regions. In addition, both couplers are integrated on the same devices, facilitating the design. A prototype of the CAD model has been 3D-printed (Up! printer), on ABS (Acrylonitrile-Butadiene-Styrene) material (3D Fila Print). The resulting connector is shown in Fig. 3(c).

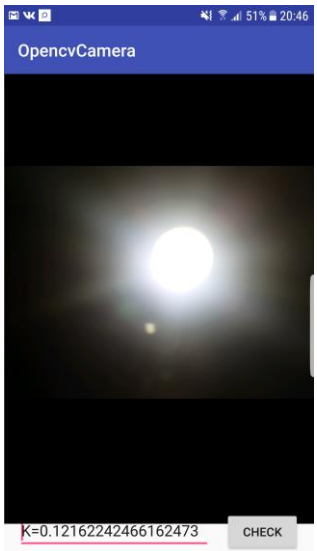

Fig. 4. Screenshot of the Android app developed in Java.

Intensity measurements were performed through a customized mobile application (app), specifically designed for Android. The mobile app was developed in Java for Android 7.1.1 Nougat operating system and based on the main features of the Open

Source Computer Vision (OpenCV) library. The application allows controlling the flashlight, adjusting the acquisition mode (which removes camera's built-in exposure compensation and sets the needed exposure time), acquiring the images and analyzing them. Acquired images are compared with the reference that depicts the intensity of a light transmission at its maximum, computed prior to the exposure to H_2S. Since we are interested only in the difference between intensities, both the camera and reference images are converted to the gray scale (8-bit quantization). Then, it calculates the intensity of the image as the sum of all pixel values, after performing dark subtraction by normalizing for the background level. The graphic user interface of the app is shown in Fig. 4. The app controls the flashlight, sets the parameters of the camera including the exposure time, disables the auto-focus, aligns the image to the center, and compares the new image to the reference. The app can either operate with a single picture, with a repeated set of pictures, or acquire the image in video mode. The image alignment is performed by calculating the 2-dimensional correlation of reference and measured image, editing the OpenCV *compareHist* routine: this allows compensating for slight motions of the connector when the smartphone is handheld.

Fig. 5. Image detected on the smartphone, in reference conditions, for different values of camera exposure time (ISO ranging from 100 to 12800).

Fig. 5 shows the detected images, in reference condition (i.e. no exposure to H_2S) for different values of exposure time (ISO of the camera). For low values of exposure time (ISO = 100-400) the image brightness does not reach saturation level, approaching the saturation for ISO = 800. For ISO ≥ 1600, the image brightness is saturated; for high value of exposure time (ISO = 6400-12800), the image alignment routine is more vulnerable to small motions of the connectors, due to the long integration time. Based on this analysis, we choose ISO = 3200 as the best trade-off: the image is saturated in the center, facilitating the image-alignment routine, but the effect of camera flares and connector motions is reduced.

A proof of principle was demonstrated by exposing the sensor system to the H_2S gas in the laboratory and analyzing acquired intensity values. The hydrogen sulfide was produced by mixing melted paraffin with sulfur. The solidified mixture was then heated to produce H_2S gas. The Ag-coated POF was indirectly exposed to H_2S; as shown in [7-8], the sensor reduces its transmittance as a function of the H_2S dosimetry (which is function of H_2S concentration and exposure duration).

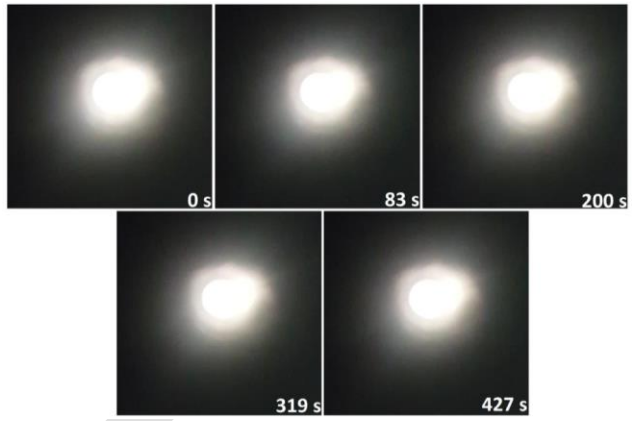

Fig. 6. Pictures of the images acquired on the smartphone camera, acquired with the Android app and aligned, for different values of exposure to H_2S (0 s, 83 s, 200 s, 319 s, 427 s).

The behavior of the POF sensor, having 4 cm sensing region, is illustrated in Fig. 6. As the H_2S deposits on the fiber and triggers the reaction, we observe an increase of the optical losses through the sensing region. The intensity of the image, detected on the camera, decreases as shown in the figure. The saturation level, observed in the brightest points, maintains a saturation level; on the other side, the decrease of intensity can be observed in the contour of the image. A MPEG-4 video showing the detected image over the whole 427 s of exposure to H_2S is shown in Supplementary Files (after reducing resolution from initial 1920×1080 to 854×480).

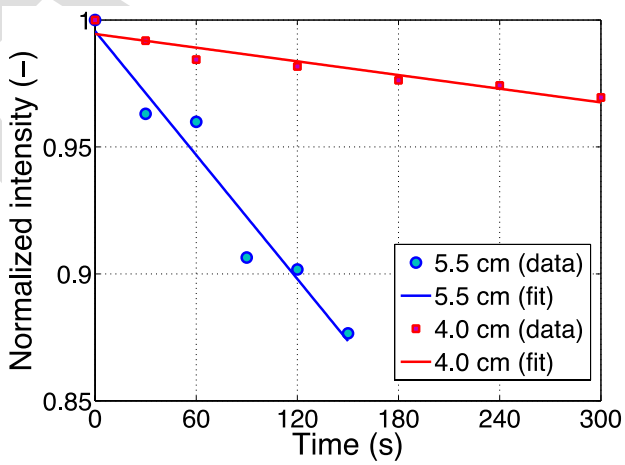

Fig. 7. Experimental results obtained for two Ag-coated POF sensors, having length 5.5 cm and 4.0 cm. Both experimental data and linear fits are reported. Intensity is obtained as the sum of all aligned pixels on camera, and normalized for the reference value.

Experimental results are reported in Fig. 7, for two POF sensors having length 5.5 cm and 4.0 cm. The longer sensor exhibits a significant reduction of light intensity in a relatively short time, when exposed to H_2S. The intensity reduction exhibits a nearly linear trend, with slope –4.9%/minute, for 150 s exposure. The shorter probe shows a similar linear trend, with–0.54%/minute slope, for 300 s exposure. In comparison, no intensity variation is observed in absence of H_2S. The experimental results confirm the

validity of our system in a proof of concept, as the presence of H_2S is transduced to a different brightness on camera. Compared to [8], we tested the system for lower exposure duration and higher H_2S concentration, accelerating the Ag_2S formation.

In conclusion, we were able to successfully integrate the Ag-coated POF sensor with the smartphone and a proof of principle experiment demonstrated its ability to detect H_2S. The main advantage of the developed sensor system is that it can provide an adequate sensitivity for a relatively low cost in environmental sensing, and despite operating on a smartphone it can enable remote sensing. Compared to [1], which requires the precision alignment of a diffraction grating and fiber cleaving, the investigated method encodes the entire light coupling and collection on a single element. The proposed system demonstrates extremely promising avenues for future work in the integration of high-NA fiber optic sensors and commercially available smartphones, transforming a pocket device into a powerful sensing unit with the addition of a simple 3D-printed connector. In this pilot study, the reduced number of POF sensors and the relatively high saturation of intensity on camera (which is however useful to calibrate the images and the detection method) limit the performance of the system; future efforts will aim at including basic light spatial filtering in the 3D-printed connectors, improving the intensity detection routine, compress videos for reducing data size, and export the structure to other smartphones by editing the connector CAD design. Long-term performance would significant benefit from the possibility of editing all the settings of the smartphone camera, and eventually enable a modulation of the flashlight.

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