Dye-Assisted pH Sensing Using a Smartphone

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Abstract—We report the working of a smartphone-based optical sensor for the measurement of pH level of colorless aqueous media. By integrating readily available laboratory optical components to the camera of the smartphone, we convert the smartphone into a visible spectrophotometer with spectral resolution of 0.345 nm/pixel. Evanescent light signal from the designed optical sensing setup is allowed to interact with a pH sensitive dye sample. The transmitted light signal from the sensing region is then captured by the camera of the smartphone in the form of modulated visible image spectrum. The designed sensor can detect change in pH level of medium with a resolution of 0.12 pH unit within range of 6-8 pH unit. We evaluate the repeatability of our sensor for eight consecutive trials and obtained a standard deviation ~0.015 in the transmission intensity within range of 6-8 pH units. We envision that our designed sensing technique could emerge as a low cost, portable, and robust pH sensor that has the ability to measure pH level of colorless aqueous medium with good accuracy and repeatability.

Index Terms—Smartphone, evanescent wave coupling spectroscopic sensor, absorption spectroscopy, pH.

I. INTRODUCTION

TEASUREMENT of pH level of aqueous media plays a crucial role in different fields of applications that include environmental science, biological science and in different industrial applications [1]–[4]. Different approaches are there to measure pH level of an aqueous medium, namely visual methods, potentiometric methods and spectroscopic methods. Visual methods lack accuracy while potentiometric methods are limited to non-inflammable liquids and spectroscopic methods require bulky and expensive spectrophotometer. Also, none of these methods facilitate wireless data transmission. Hence, a need for light weight, low cost and portable pH sensor with wireless data transmission feature is highly anticipated. These issues have been successfully addressed by our smartphone based pH sensing platform for measuring pH level of colorless aqueous medium suitable for in-field pH monitoring. Currently there are over 7 billion cellphone users and over 40% of them are smartphone users [5]. This device has gained ubiquity in day-to-day life of modern civilization. Smartphones are equipped with advanced multidimensional features like wi-fi, Bluetooth, ambient light sensors, good megapixel cameras, accelerometers and many more. Also iTunes and google play store offers a rich

Manuscript received May 5, 2015; revised July 15, 2015; accepted July 24, 2015. Date of publication August 25, 2015; date of current version September 30, 2015.

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Digital Object Identifier 10.1109/LPT.2015.2465132

variety of apps which can be easily downloaded and take just seconds to install. Further, smartphones provide android, iOS and windows based platform which facilitates users to develop apps in accordance to their need of applications. Considering the current scenario, researchers around the world are actively engaged in developing different types of smartphone based optical [6], [7] and electrochemical devices [8]. In most cases, camera of the smartphone has been extensively utilized for developing different optical sensing tools in the field of surface Plasmon resonance [9], biochemiluminescence [10] spectroscopy [11], microscopy [12] and other types of sensing platform for quantification of vitamin D [13] and cholesterol [14]. Hence, it can be accepted that smartphones have the potentials to evolve as the next generation analytical device. Such devices can enhance the demand of currently existing tools in terms of cost, portability and wireless data transfer enabled field-deployable functionality. Recently, we have demonstrated the working of an evanescent wave coupled spectroscopic sensor using the camera of the smartphone [15]. We demonstrated that the wavelength absorption bands of different colored dyes could be measured accurately and repeatedly through evanescent wave coupling of an internally reflected light signal from a broadband optical source. In this letter we primarily exploit the same sensing principle for measurement of pH level of a colorless aqueous media. The reliability of the designed sensor has been investigated through detection of pH level of different water samples collected from different water resources. We envision that the proposed technique could emerge as a handheld, relatively inexpensive tool for monitoring the quality of water found in different environmental bodies.

II. SENSOR DESIGN AND OPERATION

Schematic of the proposed sensor is shown in figure 1(a). Light signal from a broadband optical source (350-1050 nm, Model: LS-1, Ocean Optics) is allowed to pass through a pinhole of diameter 50 μ m. The light signal coming out of the pinhole is collimated by a plano-convex lens of focal length 73 mm. The collimated light beam then falls on the hypotenuse face of a right angled glass prism and undergoes total internal reflection. This internally reflected light beam is focused into a line beam by a cylindrical lens of focal length 50 mm. A transmission grating of 1200 lines/mm is placed at the focal plane of the cylindrical lens that disperses the beam into its constituent components. The grating is attached to the camera of the smartphone. The dispersed spectrum can be seen on the display unit of the smartphone. The presence of internal optical filter embedded with the camera module of the smartphone makes the camera to do visual detection in the wavelength range of 400-700 nm. The collimated beam at one of isosceles face of the prism undergoes total internal reflection due to which a strong evanescent field generates at the base of the prism. This evanescent field is allowed to

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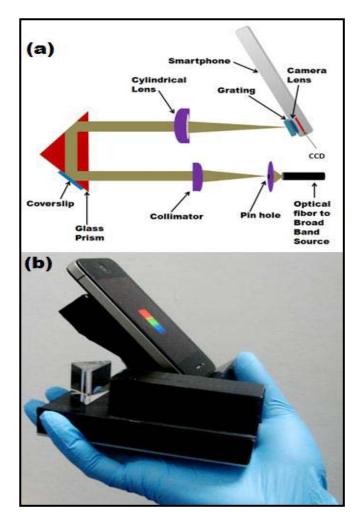


Fig. 1. (a) Schematic of the proposed sensor and (b) Snapshot of the handheld sensor excluding the broadband light source.

interact with dye-treated pH samples and the resulted modulated light signal is captured by the camera of the smartphone. Before taking the spectrum images, the iPhone camera is locked at autofocus mode (AF locked). Locking the camera at AF mode ensures focusing on a specific object located at infinite distance. To convert the pixel based information of the image sensor into corresponding wavelength value, we follow the similar procedure reported in our previous work [15]. Upon calibration, we obtain a spectral resolution of 0.345 nm/pixel. Figure 1(b) shows the handheld photograph of the designed sensor excluding the broadband source.

III. RESULTS AND DISCUSSION

In order to study the characteristics of the designed sensor we choose phenol red dye (SRL, India) as pH sensitive dye. The transition range of phenol red dye is 6.8 to 8.2. Buffer solutions of different pH value ranging from 4 to 9 in step increment of 1 pH unit were prepared using standard procedures [16]. Their pH values were measured before and after the experiment using a standard pH meter (Mettler Toledo FE20). Each buffer solution has been treated with phenol red indicator dye at concentration of 0.01%. Using a micropipette, $20~\mu l$ of dye-treated pH sample is dispensed on a coverslip (Corning glass, USA) and then attached it to the sensing region of the glass prism. The evanescent field generated at

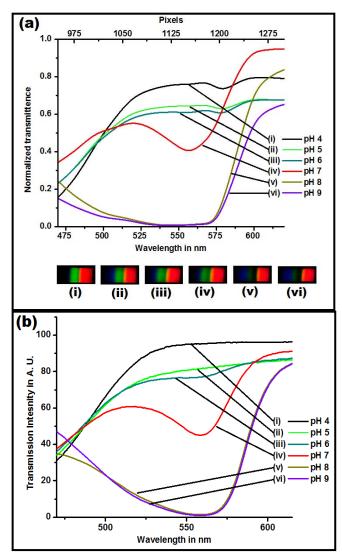


Fig. 2. Characteristic transmission plot for phenol red treated standard buffer solutions from pH 4 to 9 obtained with (a) Designed smartphone sensor, (b) Standard spectrophotometer (UV 2450, SHIMADZU).

this region interacts with the dye-treated pH sample and the resulted modulated light signal is captured by the camera of the phone.

Phenol red dye shows different level of transmission intensity at 558 nm depending on pH level of the medium. This change in transmission intensity can be correlated with pH level of the aqueous medium. Figure 2(a) shows the characteristic plots of transmission spectra of different pH media normalized with respect to the characteristic plot of bare optical spectrum from 470 nm to 620 nm. Inset figures show the photo images of the captured transmission spectra of dyetreated different pH buffer medium of pH value 4, 5, 6, 7, 8 and 9 pH unit respectively. The captured image spectra have been processed using an open access software ImageJ to obtain a intensity vs. pixel profile of the captured spectrum. Assuming a linear relationship between pixel and wavelength along dispersive direction, a MATLAB code is written to obtain the spectrum profile in wavelength scale. At 558 nm phenol red dye shows a significant absorption which increases with the increase in pH value of the solution. The absorption at 558 nm becomes significant when the pH of the medium

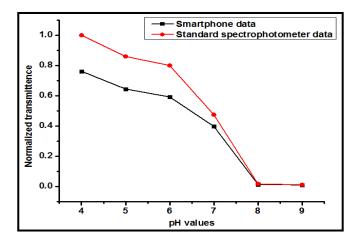


Fig. 3. Comparison of smartphone sensor response to that of a standard spectrophotometer.

becomes greater than 6 pH unit which has been clearly demonstrated by our designed sensor. To validate the results obtained with our smartphone sensor, we measure the absorption band of the same samples using a standard spectrophotometer (UV 2450, SHIMADZU). Figure 2 (b) shows the characteristic transmission plot of the same samples using the standard spectrophotometer. Figure 3 shows the variation of transmission intensity measured using our designed smartphone sensor with respect to a standard spectrophotometer. The response of our sensor is nearly matching with that of the laboratory grade spectrophotometer.

From the characteristic transmission plots we infer that our designed sensor shows good linearity within pH range of 6 to 8. Since pH values of most of the environmental water bodies are generally found in this range, we envision that the proposed sensing technique could be suitable for monitoring of pH values of different water bodies viz. lakes, rivers, ponds and ground water.

To test the performance of our designed smartphone sensor, we collect water samples from 3 different locations of Tezpur University campus. The collected water samples have been filtrated using Whatmann filter paper to remove other particulates which may interfere with the experimental procedure. The pH value of the collected water samples were measured to be 7.52, 7.68 and 7.87 pH unit. Additionally, we have prepared water samples of pH value 6.5, 7.13, 7.25 and 7.35 pH unit by using 0.1N NaOH and 0.1N HCl in the laboratory environment. 1.5 ml of collected water samples and the laboratory-prepared water samples have been treated with phenol red indicator dye at final concentration of 0.015%. Figure 4 (a) shows the characteristic plot of the transmission spectra of phenol red-treated water samples along with the dye-treated standard buffer samples of pH value 6 and 8 respectively. Figure 4 (b) shows the transmission plot of the sample solutions (6, 7, 7.52, 7.68, 7.87 and 8 pH unit) as measured by the standard spectrophotometer. The designed sensor yields a distinguishable transmission intensity curve as pH value of the aqueous medium is varied in the range 6-8 pH unit. The sensor is unable to resolve any variation below 0.12 pH unit. This signifies that with the present optical set-up and the considered pH sensitive dye, the proposed sensor can perform up to resolution of 0.12 pH unit. We investigate the repeatability response of our sensor

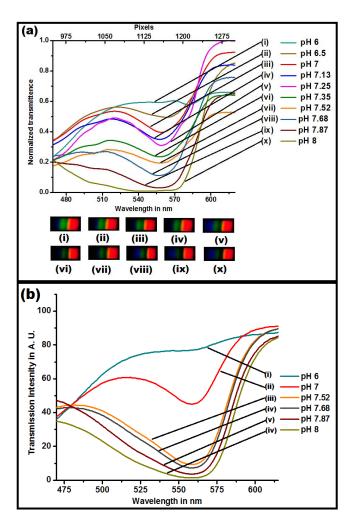


Fig. 4. Characteristic transmission plot (normalized w.r.t the source) for phenol red treated standard buffer solutions (6 and 8 pH unit) and random water samples obtained with (a) Designed smartphone sensor, (b) Standard spectrophotometer (UV 2450, SHIMADZU).

for 8 consecutive trials and obtained a standard deviation \sim 0.015 in transmission intensity within range of 6-8 pH units. As per our claim, the linearity of our designed sensor is well defined within the range of 6 to 8 pH unit. Figure 5 shows linear response as showen by our designed sensor within 6 to 8 pH unit.

A correlation coefficient of 0.956 is obtained that shows good linear behavior of the smartphone sensor suitable for measuring pH of fresh water bodies. By doing the linear fitting, regression equation governing the empirical relationship between the pH and intensity for our designed sensor is found to be

$$pH = \frac{2.4855 - I}{0.3063} \tag{1}$$

where, I is the normalized transmission intensity value at 558 nm as captured by the camera of the smartphone. Using equation (1) we estimate the pH values of the considered samples and observe that pH values of all the considered samples are varying within the range of 0.01-0.15 pH unit from the actual values as measured by the standard pH meter. The accuracy of the designed sensor is found to be \pm 0.10 pH unit.

Thus, with the considered pH indicative dye and using the relation (1) we can determine pH value of any random

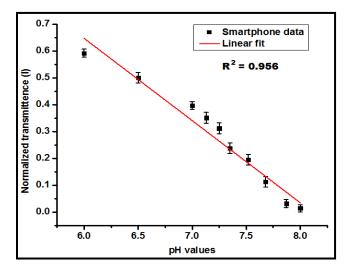


Fig. 5. Linear fitted curve for transmission intensity vs. pH values from 6 to 8 pH unit.

water samples within pH range of 6 to 8 pH unit. Assuming linear response of the designed sensor over 6-8 pH unit, the pH sensitivity, S_{pH} of our sensor in the pH range of 6 to 8 pH unit is defined as

$$S_{pH} = \frac{\Delta I}{\Delta pH} \tag{2}$$

Here $\Delta I = 0.578$, change in transmission intensity (normalized w.r.t the broadband source) between pH value 6 to 8 pH unit and $\Delta pH = 2$ pH unit, difference between these two pH values.

Using this relation the sensitivity of our designed sensor is found to be 0.289/pH unit which shows the proposed pH sensor exhibits good level of sensitivity over a pH range of 6 to 8. To measure the pH level of colorless aqueous media below 6 pH unit, dyes such as bromocresol green (transition range- 3.8 to 5.4) can be used. The overall cost involved for making the entire device excluding the smartphone is approximately \$ 250. The dimension of the sensor in terms of its length, breadth and height is 11.5 cm, 10 cm and 9 cm respectively. The plot of transmission intensity vs. pixel index can be directly done in the phone itself by using open access software image J (IJ_mobile) which can be easily downloaded from google play store for android platform based smartphones. There are two types of color present in water [17] namely true color and apparent color. Dissolved chemicals gives true color which cannot be separated by filtration but apparent color caused by the suspended colloids can be separated by filtration. Thus, due to chromaticities caused by dissolved chemicals the peak absorption condition of the dyetreated water sample gets affected. This can be avoided by choosing dyes which are less sensitive to interference caused by dissolved chemicals. At present, the choice of phenol red dye can cause some discrepancy in measuring pH of the aqueous samples that limits the use of this dye for performing fully field-deployable pH sensing investigation.

IV. CONCLUSION

A smartphone based pH sensor capable of measuring pH level of colorless aqueous media is proposed.

The performance criteria investigated for the designed sensor shows good accuracy, reproducibility and resolution up to 0.12 pH unit or better. We have successfully demonstrated the ability of our smartphone pH sensor for measuring a small variation of pH of different water samples with good degree of resolution and sensitivity. Because of its compact size our designed sensor is handy and is useful for different in-field applications. The existing mobile network can be utilized for transferring pH information of the water bodies to anywhere in the world. We envision that the proposed sensor could emerge as an inexpensive alternative to the presently commercially available pH sensing investigation.

ACKNOWLEDGEMENT

P. Nath is indebted to B. T. Cunningham for valuable guidance on similar line of work during his visit to the University of Illinois at Urbana Champaign USA during 2011-12.

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