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Development of inexpensive device for methanol detection in hand sanitizer gel using manganese-doped zinc sulfide quantum dots modified by N-methylpolypyrrole

Sophanat KHENTHAPHAK[2], Pakorn JULEANG[3], Wanida WONSAWAT[4], Orawon CHAILAPAKUL[2], and Eakkasit PUNRAT[1,*]

[1] *Department of Chemistry, Faculty of Science, Ramkhamhaeng University, Bang Kapi, Bangkok 10240, Thailand*
[2] *Electrochemistry and Optical Spectroscopy Center of Excellence, Department of Chemistry, Faculty of Science, Chulalongkorn University, Pathumwan, Bangkok 10330, Thailand*
[3] *Electronics Technology Department, Faculty of Science, Ramkhamhaeng University, Bang Kapi, Bangkok 10240, Thailand*
[4] *Department of Chemistry, Faculty of Science and Technology, Suan Sunandha Rajabhat University, U-Thong Nok Road, Bangkok 10300, Thailand*

***Corresponding author e-mail:** eakkasit.p@rumail.ru.ac.th

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Digital-image colorimetry;
Hand sanitizer gel

Abstract

A method for methanol detection by an inexpensive device using a nanomaterial modified by N-methylpolypyrrole (NMPPY) has been developed. Manganese-doped zinc sulfide quantum dots (Mn/ZnS-QDs) were synthesized and then characterized by a fluorescence spectrophotometer to study their spectroscopic properties. Mn/ZnS-QDs were modified with NMPPy and studied by digital-image colorimetry to optimize conditions for methanol detection. A 2 mL of 3000 $mg\cdot L^{-1}$ Mn/ZnS-QDs modified with 300 µL of 1000 $mg\cdot L^{-1}$ of NMPPy was chosen to be a detecting reagent for methanol determination. Under the optimum conditions, the linear range was found to be 2%v/v to 50%v/v of methanol with R-square of 0.9434 and the sensitivity of 3.569×10^{-3} $(\%v/v)^{-1}$, whilst the limit of detection (LOD) was 19.5%v/v. The selectivity of this method was also studied with several solvents; it was proven selective for methanol. Furthermore, a prototype device with simple and inexpensive has been created. The analytical performances were studied; the linearity of methanol detection was found in the range of 20%v/v to 80%v/v with R-square of 0.9918 and the sensitivity of 3.38×10^{-3} $(\%v/v)^{-1}$. Finally, the newly developed device was applied to analyze samples of hand sanitizer gel by digital-image colorimetry with acceptable results.

1. Introduction

Methanol or methyl alcohol (CH_3OH), which is a light, colorless, and volatile liquid, is an organic compound with a hydroxyl group. Methanol is often used as an organic solvent for fuel cells, and as a precursor for the synthesis of plastics, drugs, and organic compounds, especially formaldehyde. Thus, methanol is significantly essential for science, medicine, energy, and fuel. Furthermore, it is frequently employed in a variety of industries, including paint, furniture, food, wood, heavy metals, electronics, and automobiles [1]. However, methanol is extremely poisonous to humans and can have an immediate toxic effect on the body, such as headaches, nausea, and conjunctivitis, especially on the respiratory, visual, and digestive systems as well as the central nervous system, which can be fatal [2,3]. Exposure to methanol inside the body can be extremely dangerous. The methanol concentration of more than 500 $mg\cdot L^{-1}$ and 1,000 $mg\cdot L^{-1}$ in the blood is harmful to the body and cause death, respectively. Therefore, the determination of methanol is crucial.

Coronavirus disease 2019 (COVID-19) is a virus-borne infection caused by the Severe Acute Respiratory Syndrome Coronavirus-2 (SARS-CoV-2). Patients infected with SARS-CoV-2 must be evaluated and treated differently than patients infected with other coronaviruses [4]. At the present, COVID-19 has been a major issue in many nations throughout the world, and the epidemic has been continuing to spread rapidly. However, people must adapt to “The New Normal”, which includes social withdrawal, working from home, and online participation. Therefore, personal protective equipment for anti-COVID-19 is also very essential. As a result, there is an urgent requirement for personal protection items, including masks, hand soap, and hand sanitizer gel [5].

An alcohol-based hand sanitizer gel is a product for washing hands instead of washing hands with soap and water because alcohol is effective against bacteria and viruses, including a novel coronavirus (COVID-19). The alcohol-based hand sanitizer gel must contain a minimum of 60% alcohol by weight to effectively disinfect hands and its major components must be ethanol or propanol, which are benign to the body. Due to the increased demand for hand sanitizer gel, there are several fake alcohol gels containing cheaper substitutes like methanol, which is an extremely dangerous substance as mentioned above.

As a result, the analysis for categorizing the types of alcohol and contamination is essential for screening hand sanitizer gel and getting rid of non-standard alcohol gel for the consumers’ safety. Typical techniques for the determination of methanol are chromatographic techniques [6], electrochemical techniques [7], spectroscopic techniques [8], enzymatic techniques [9] or other gas sensors [10], which have high operation costs and complicated procedures in a laboratory with a long analysis time. Therefore, the detection of methanol would be developed for low operational costs.

Quantum dots (QDs) or semiconductor nanocrystals (NCs) are widely used as measurement sensors, especially in medical and electronic equipment [11] because quantum dots have a variety of unique optical and chemical features depending on the size and shape of the particles [12], their advantages are high sensitivity, prolonged fluorescence lifetime, simplicity in synthesis, and ease of study [13]. Moreover, Mangenese-doped ZnS Quantum dots modified ligand by capped with N-acetyl-L-cysteine were firstly prepared by hydrothermal methods and used as phosphorescence probes for detecting L-ascorbic acid. It was found that these QDs probes could efficiently quench and have high selectivity to L-ascorbic acid [14].

According to the unique properties of quantum dots, Abbasi and co-workers [15] synthesized a novel CdS quantum dots/N-methyl polypyrrole (CdS QDs/NMPPY) hybrid as optical sensors and reported that their materials resulted in a significant change in the fluorescence sensing properties toward nitroaromatic compounds. Interestingly, the level of picric acid in actual water samples was effectively determined using the proposed CdS QDs/NMPPY sensor. Furthermore, a new fluorescence probe using a ZnS:Mn^{2+} quantum dot and soluble N-methylpolypyrrole (NMPPy) hybrid was employed as a fluorescence switchable sensor for the direct detection of methanol in an aqueous solution. It was found that this hybrid was reported to be highly sensitive, highly selective, and to have a very good detection limit of 1 mM with linearity in the concentration range of 25 mM to 230 mM (0.1%v/v to 0.9%v/v) in an aqueous solution. Finally, it was effectively used to determine the amount of methanol in actual samples of alcoholic beverages [16].

In this research, a device for methanol detection has been developed using the principles of spectroscopy using manganese-doped zinc sulfide quantum dots (Mn/ZnS-QDs), modified by N-methylpolypyrrole polymer (NMPPy). Then they were analyzed by digital-image colorimetry for the detection of methanol. Under the optimal conditions, this newly developed device has been a simple, inexpensive, easy-to-build, and portable device for methanol detection in hand sanitizer gel to distinguish it from toxic alcohol.

2. Experimental

2.1 Chemicals and apparatus

Manganese chloride ($MnCl_2$), zinc chloride ($ZnCl_2$), ammonium persulfate ($(NH_4)2S_2O_8$), N-methylpyrrole and tris-HCl were purchased from Sigma-Aldrich (analytical grade, Germany). Sodium sulfide (Na_2S) was purchased from PanReac AppliChem ITW Reagent (technical grade, Spain). Acetonitrile (CH_3CN) and chloroform (CH_3Cl) were purchased from Merck Millipore (analytical grade, Germany). Sodium chloride (NaCl) was purchased from Ajex Chemical (analytical grade, Australia). All working solutions were prepared and diluted by deionized water.

2.2 Synthesis of Mn/ZnS-QDs

Mn/ZnS QDs were synthesized by a chemical precipitation method [17]. The effect of the reaction temperature was studied at room temperature, 50, 80, 100, and 120°C. Briefly, 10 mL of 0.5 M tri-sodium citrate, 10 mL of 0.01 M $MnCl_2$, and 10 mL of $ZnCl_2$ were mixed and stirred for 10 min. After that, 10 mL of 1.0 M Na_2S was slowly added drop-by-drop into the mixture at a considered temperature for 3 h, and then the mixture was continuously stirred for 3 h at the same temperature. Then, a colloidal suspension of Mn/ZnS QDs was obtained and centrifuged. After centrifugation, the precipitates were separated and then redispersed into 40 mL of distilled water.

2.3 Synthesis of NMPPy polymers

The procedure for the synthesis of NMPPy was mentioned in the literature [18]. Briefly, 103 mg of N-methylpyrrole monomer and 53 mg of sodium dodecyl benzene sulfonate were added to 8.75 mL of a solvent containing acetonitrile and deionized water in a ratio of 60:40. After heating up to 60°C, 1.25 mL of 165 mg of ammonium persulfate in the same solvent were added to the solution under continuous stirring at 60°C for 7 h; the polymerization reaction occurred. The NMPPy polymer was extracted by adding 5 mL of chloroform and 1 g NaCl. The NMPPy with a dark-brown color in the water phase was separated and then remove the solvent by evaporation. The NMPPy polymer was obtained as a solid product.

2.4 Methanol detection by digital-image colorimetry (DIC)

To study the color of the solution by digital-image colorimetry (DIC), a light box and a black light box, as shown in Figure 1 were made for photography using a smartphone (iPhone5, Apple, USA). The light box, which is used to calibrate the smartphone's camera, has white-light-emitting diodes, while the black light box with two black light lamps was used for luminescence studies. The position of a cuvette was set and locked. The digital images were taken, and then analyzed by the ImageJ program. In addition, a fluorometer (Cary Eclipse, Agilent, USA) was used for the study of the fluorescent spectra.

To determine the concentration of methanol by DIC, 2 mL of 3000 mg·L^{-1} Mn/ZnS-QDs suspension, 50 mM Tris Hydrochloride buffer (TBS, pH 8.5), 300 µL of 1000 mg·L^{-1} N-methyl polypyrrole polymer (NMPPy), and 1 mL of sample were pipetted and mixed in a test-tube before being poured into a cuvette to be photographed

Figure 1. A light box (left) and a black light box (right) used for digital-image colorimetry.

by the smartphone under the black light. Before taking a photograph with the smartphone, the Yamera application was used for manually setting the white balance with an 18% gray card under the light box, and then fixing the exposure to control the brightness. The focus distance was also fixed with the black light box. The digital images were analyzed for red to green color intensity (R/G) by the ImageJ program.

2.5 Prototype device for methanol detection by DIC

The design and invention of the prototype device aim to create and develop a small, easy-to-use, and inexpensive device using an electronic circuit board (UNO, Arduino, China), which can be easily written to or connected to control modules as illustrated in Figure 2. There were 2 detectors: which were a light intensity detector and an RGB (Red, Green, and Blue) color component detector. These detectors were installed perpendicular to a light source that can be turned on or off independently of other controlling factors, allowing the user to turn it off to prolong the service life. The value of the result was shown on the LED display.

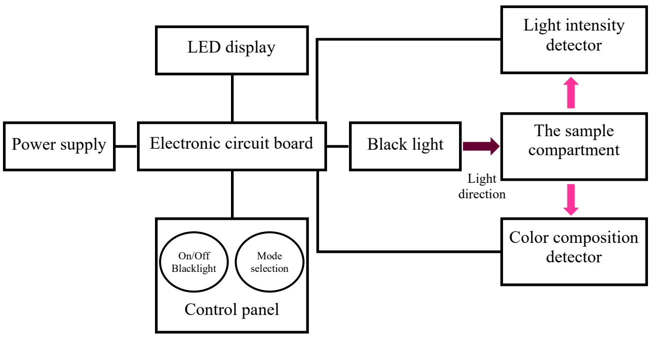

Figure 2. Diagram of the prototype device for methanol detection.

3. Results and discussion

3.1 Effect of temperature and reaction time for synthesis of Mn/ZnS-QDs

The fluorescence properties of the synthesized Mn/ZnS-QDs at various temperatures of room temperature, 50, 80, 100, and 120°C were investigated by a fluorescence spectrophotometer. The wavelength of excitation and emission can be confirmed as shown in Figure 3. The excitation wavelength was found to be between 308 nm and 312 nm, and the emission wavelength was found to be between 413 nm and 426 nm, indicating the existence of Mn/ZnS-QDs. This is related to other published research [16], which stated the excitation wavelength to be 325 nm and the emission wavelength is 420 nm. The fluorescence intensities are shown in Table 1. The maximum temperature for the synthesis used in this work is 120°C because the solution was dried at a higher temperature than 120°C.

To study the effect of reaction time on the synthesis of Mn/ZnS-QDs, photographs of the Mn/ZnS-QDs suspension were taken every hour under the black light, and their red and blue channel colors were analyzed using the ImageJ program as shown in Figure 4. It was found that the synthesized Mn/ZnS-QDs suspension at room temperature and 50°C was blue with a red to blue intensity ratio of less than 1.00, while the colors of those at 80°C and 100°C were pink with an intensity ratio in the range of 1.00 to 2.00. Finally, the red-orange suspension using 120°C was obtained at the higher intensity ratio. It was found that a reaction time of 1 to 5 h provided a similar color solution, so using a short reaction time of 1 h is enough to synthesize Mn/ZnS-QDs with a good response under the black light. Therefore, the optimum conditions for the synthesis of Mn/ZnS-QDs were a temperature of 120°C and an hour of reaction time.

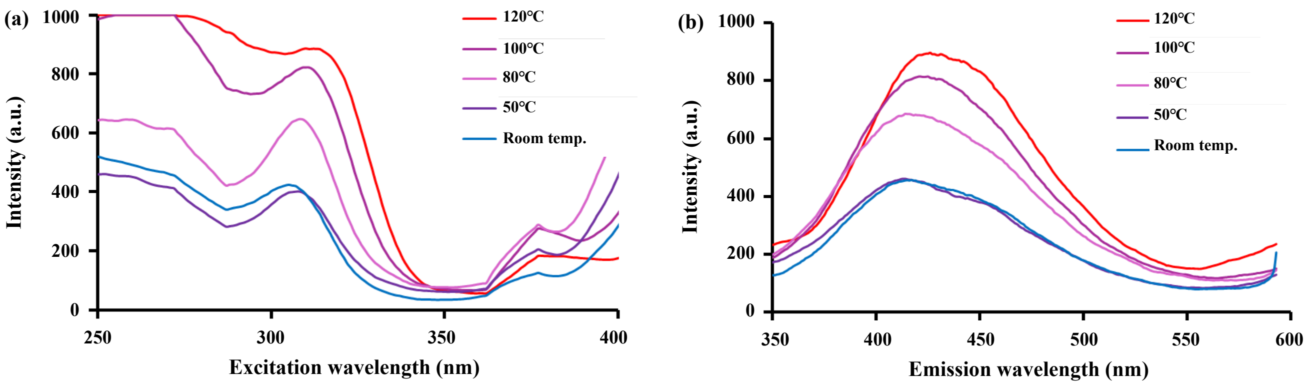

Figure 3. The fluorescence spectra of the synthesized Mn/ZnS-QDs at various temperatures, showing the relationships between the fluorescence intensity with the excitation wavelength (a) and the emission wavelength (b).

Table 1. Excitation and emission wavelength and intensity of the synthesized Mn/ZnS-QDs at various temperatures.

Temperature	Excitation		Emission	
	Wavelength (nm)	Intensity (au)	Wavelength (nm)	Intensity (au)
Room	308	411	413	455
50°C	308	401	413	461
80°C	310	645	421	686
100°C	312	822	426	815
120°C	308	684	413	897

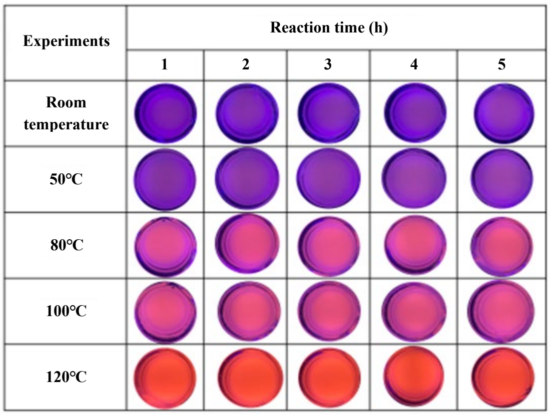

Figure 4. The photographs of the synthesized Mn/ZnS-QDs suspension under the black light with various reaction times and temperatures at room temperature, 50, 80, 100, and 120°C.

3.2 Effect of concentrations of Mn/ZnS-QDs

The optical properties of the Mn/ZnS-QDs suspension in 50 mM Tris Hydrochloride buffer (TBS, pH 8.5) with various concentrations, which were 10, 25, 50, 75, 100, 250, 500, 750, 1000, 2000, and 3000 mg·L^{-1}, were investigated by digital-image colorimetry (DIC) using the smartphone (iPhone5) under the black light with four replicates as shown in Figure 5. The suspension at a concentration of over 3000 mg·L^{-1} is not homogeneous; some precipitates settled at the bottom of the vial. It was found that the color solution of the colloid suspension was redder with the increased concentration when it was analyzed the red intensity by the ImageJ program. Moreover, the lowest concentration of Mn/ZnS-QDs suspension that gave the signal with significantly difference from the blank's signal, which was obtained from 3 times of signal to noise ratio (3S/N) of blank responses (n=20), was found to be a concentration of 25 mg·L^{-1}. However, for the obvious color change in subsequent experiments, the high concentration of 3000 mg·L^{-1} Mn/ZnS-QDs was selected to be a detecting reagent for analysis.

3.3 Effect of NMPPy on fluorescent properties of Mn/ZnS-QDs

A 3 mL of 3000 mg·L^{-1} Mn/ZnS-QDs suspension in 50 mM TBS (pH 8.5) was modified by adding 1 mL of 1000 mg·L^{-1} N-methyl polypyrrole polymer (NMPPy). Then, the photograph was taken by using the smartphone under black light and compared with non-modified Mn/ZnS-QDs for four replicates. It was found that NMPPy has the effect of quenching with the Mn/ZnS-QDs by the reaction mechanism of the sulfonate groups (S=O groups) in sodium dodecyl benzene sulfonate (SDBS) of NMPPy chains, which is micelle encapsulated the polymer coordinate with zinc and manganese of the surface area in the Mn/Zn-QDs. It can cause fluorescence resonance energy transfer (FRET) from aggregations of the Mn/ZnS-QDs [19] and electron/charge transfer [20]. To consider the color of these solutions, it was clearly observed with the naked eyes that the color of the Mn/ZnS-QDs/NMPPy hybrid changed from red to white as shown in Figure 6.

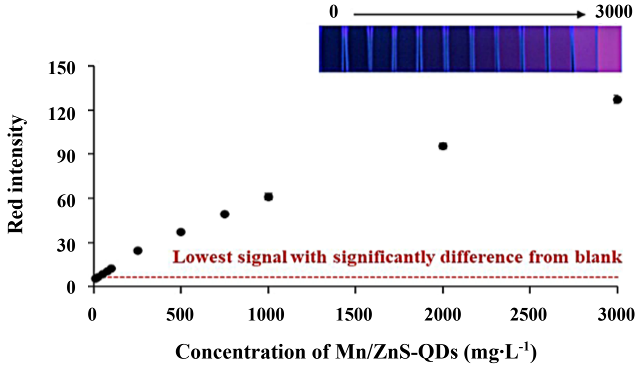

Figure 5. The relationship between the various concentrations and the red intensity analyzed by the ImageJ program, and the photograph of 0 mg·L^{-1} to 3000 mg·L^{-1} Mn/ZnS-QDs suspension in 50 mM TBS (pH 8.5) under the black light (inlet).

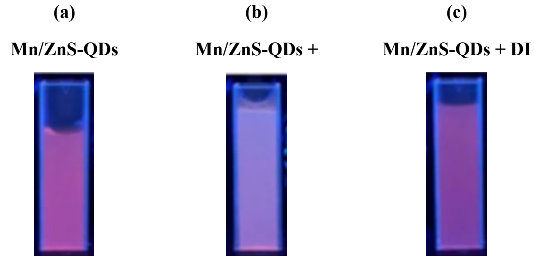

Figure 6. The photographs under the black light of (a) 3000 mg·L^{-1} Mn/ZnS-QDs suspension, (b) 3000 mg·L^{-1} Mn/ZnS-QDs with 1000 mg·L^{-1} NMPPy, and (c) 3000 mg·L^{-1} Mn/ZnS-QDs with deionized water.

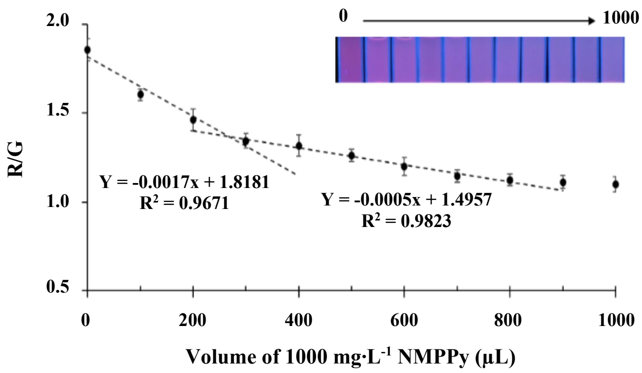

Figure 7. The relationship between the ratio of red to green color intensity (R/G) and the various volumes of 1000 mg L^{-1} NMPPy added to the 2 mL of 3000 mg L^{-1} Mn/ZnS-QDs suspension in 50 mM TBS solution (pH 8.5), and the photograph of the solutions under the black light (inlet).

The concentration of 1000 mg·L^{-1} NMPPy was selected as a detecting reagent to optimize the amount of NMPPy for quenching the fluorescence properties of the Mn/ZnS-QDs suspension. A volume of 2 mL of the 3000 mg·L^{-1} Mn/ZnS-QDs suspension in 50 mM TBS solution (pH 8.5) was pipetted into a test tube before adding with the various volumes of NMPPy, which were 0, 100, 200, 300, 400, 500, 600, 700, 800, 900, and 1000 µL, with four replicates. The ratio of red to green color intensity (R/G) with the various volumes of NMPPy was analyzed as shown in Figure 7. The ratio of red to green color intensity with the various volumes of NMPPy was divided into 2 linear ranges. The range of 0 µL to 300 µL had a sensitivity of -1.677 mL^{-1} with R-square of 0.9671, while the range of 300 μL to 800 μL had a sensitivity of -0.479 mL^{-1} with R-square of 0.9823. The optimized volumes of NMPPy should have more sensitivity with the high slope, so it could be concluded that the optimum volume of NMPPy was 300 μL.

3.4 Linear range and limit of detection (LOD) of the methanol detection

The methanol standard solutions at various concentrations of 0, 2, 4, 8, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 %v/v in 50 mM TBS solution were determined by NMPPy-modified Mn/ZnS-QDs via DIC in the optimum conditions. The relationship between the ratio of red to green color intensity (R/G) and the various concentrations of methanol shown in Figure 8 was revealed that the linear range was found in the range of 2%v/v to 50%v/v with R-square of 0.9434 and the sensitivity of 3.569×10^{-3} $(\%v/v)^{-1}$.

The limit of detection (LOD) of the methanol detection was obtained from the standard deviation of R/G of the blank solution (50 mM TBS pH 8.5) for 20 times (3S/N). The LOD of the proposed method was found to be 19.5%v/v methanol.

3.5 The selectivity of the proposed method of methanol detection

The selectivity of methanol for interaction with NMPPy-modified Mn/ZnS-QDs occurred because methanol has a small dimensionality and a high permeability coefficient [21], so it can well penetrate into the structure of NMPPy-modified Mn/ZnS-QDs that can replace and release NMPPy for interaction with the surface area of Mn/ZnS-QDs, leading to the optical properties of Mn/ZnS-QDs coming back to the amount of methanol. The proposed method was investigated by comparing results with the other solvents, which were ethanol, n-propanol, i-propanol, and acetonitrile by digital-image colorimetry (DIC) using NMPPy-modified Mn/ZnS-QDs. A 1 mL of 70%v/v of each solution was examined with the optimized conditions. Then the photograph was taken using the smartphone under the black light. The digital images were analyzed the color intensity by the ImageJ with four replicates. The results are shown in Figure 9. The result of methanol had the highest R/G intensity of 1.6, while the R/G intensities of the other solvents were all close to the blank solution at 1.5. Therefore, it could be concluded that the proposed DIC method using NMPPy-modified Mn/ZnS-QDs was good selective for methanol detection.

3.6 The methanol detection by the prototype device

The prototype device was invented by connecting designed modules to an electronic circuit board (UNO, Arduino, China), as shown in Figure 2. The board was then covered with a black plastic box created using a 3D printer to block outside light interference, as shown in Figure 10. This device can be used in any 220 V household with a power off/on switch at the wires. The LED display has two operating modes: one for detecting light intensity, and another for detecting RGB color components. Each light intensity is displayed like a gray scale in digital-image colorimetry (DIC) in the first mode. For the second mode, the color components of RGB are displayed as a color temperature, a red value (R), a green value (G), a blue value (B), and a color clarity (C). According to the light source, it can be turned on or off separately from other controlling variables, allowing the user to turn it off to prolong the service life.

The prototype device was investigated with various concentrations of methanol standard solution, including 0, 20, 40, 60, 80, and 100 %v/v in 50 mM TBS solution. A 1 mL of each standard solution was examined under the optimized conditions, mixed, and shaken via the vortex mixer before being poured into a cuvette and tested with the prototype device. The red value (R), green value (G), and blue value (B) were captured as part of the color component measurement mode. Then, the calibration curve was interpreted in R/G, R, G, and B to determine the appropriate factor for the detection of methanol, as shown in Figure 11. The results show some large error bars caused by small-scale intensities, which need for consideration of the slopes of each graph. It could be inferred that this device's sensor is poor quality because of its low price. It was found that the red value (R) provided the best performance for analyzing the sample's methanol concentrations; the linearity of methanol detection was found in the range of 20%v/v to 80%v/v with R-square of 0.9918 and the sensitivity of 3.38×10^{-3} $(\%v/v)^{-1}$. Therefore, it can be accepted for the prototype device and will be developed further in future work to achieve a better result.

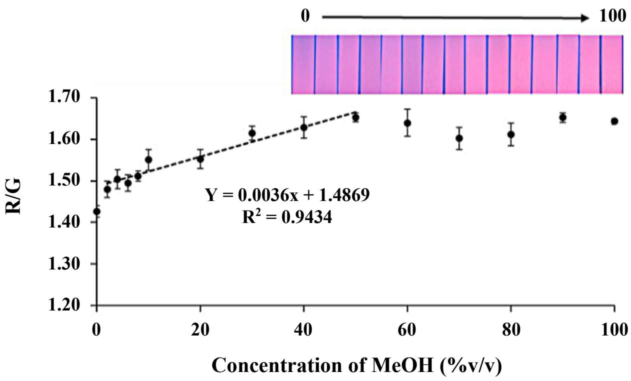

Figure 8. The relationship between concentration of methanol and the ratio of red to green color intensity (R/G) obtained by digital-image colorimetry (DIC) using NMPPy-modified Mn/ZnS-QDs, and the photograph of the solutions under the black light (inlet).

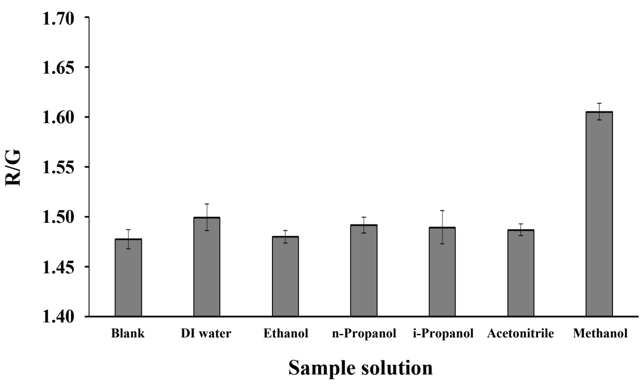

Figure 9. The ratio of red to green color intensity (R/G) of different solvents by digital-image colorimetry (DIC).

3.7 Application of methanol detection in hand sanitizer gel

The real samples from 5 brands of commercial hand sanitizer gels were Skin Soft (Sample A), Biore Guard (Sample B), Klean-C (Sample C), Alsoff (Sample D), and Virulex (Sample E), with an ethanol component ranging from 70%v/v to 79%v/v. A 1 mL sample of each hand sanitizer gel was investigated with this developed method, and then the photograph was taken using the smartphone under the black light. The digital images were analyzed the color intensity by the ImageJ program with four replicates, compared with the blank solution (50 mM TBS pH 8.5) as shown in Table 2. It was found that none of the hand sanitizer gels contained methanol because the R/G ratios were not significantly different from one of the blank with a confidence interval of 95%.

Moreover, a 1 mL sample of each sample spiked 30%v/v of methanol was investigated by this proposed method. The results are shown in Table 2, as well. According to the R/G of the non-spiked blank, the R/G signal for the LOD, which is the blank signal plus 3 times its standard deviation, was 1.520. It was found that the R/G of all spiked samples except the sample C was more than 1.520. Therefore, it can be promised that this proposed method can be used to detect methanol in hand sanitizer gel, but the procedure for sample preparation needs to be developed to reduce interference in the future.

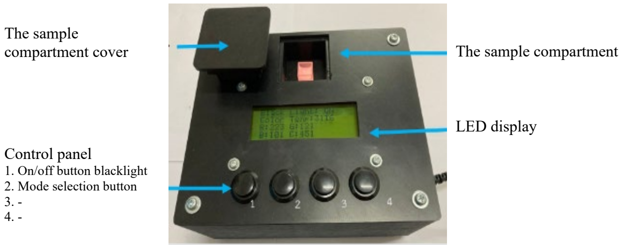

Figure 10. The prototype device for the proposed method of methanol.

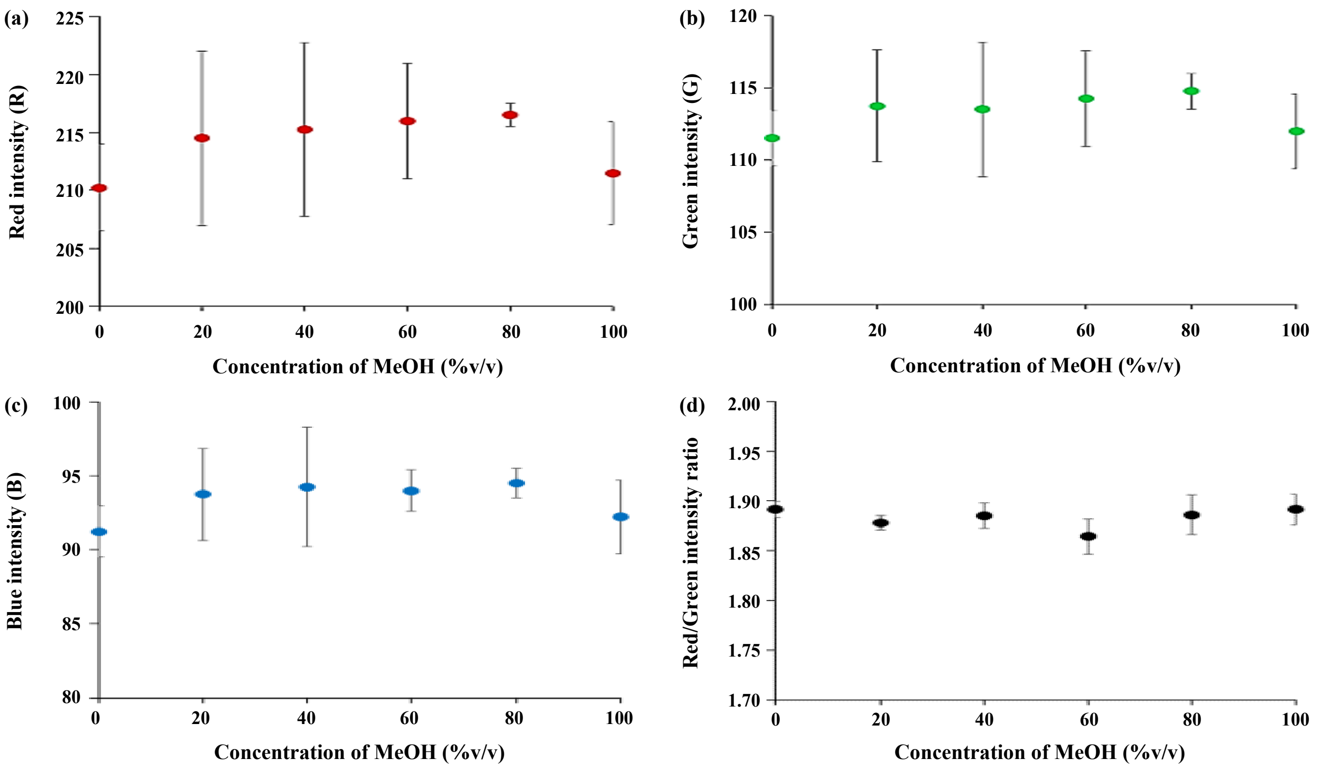

Figure 11. Calibration curves of methanol detection concentrations 0, 20, 40, 60, 80 and 100%(v/v) with the prototype device by showing the dependent variable (a) red, (b) green (c) blue and (d) ratio color intensity red/green.

Table 2. The ratio of red to green color intensity of methanol detection in hand sanitizer gels, comparing non-spiked sample and 30 %v/v methanol spiked sample by digital-image colorimetry (DIC).

Sample solution	R/G	
	Non-spiked sample	30%v/v methanol spiked sample
Blank	1.495 ± 0.005	1.527 ± 0.001
Sample A	1.445 ± 0.017	1.582 ± 0.016
Sample B	1.416 ± 0.010	1.535 ± 0.005
Sample C	1.397 ± 0.008	1.508 ± 0.019
Sample D	1.438 ± 0.021	1.576 ± 0.021
Sample E	1.467 ± 0.007	1.539 ± 0.033

4. Conclusions

Manganese-doped zinc sulfide quantum dots (Mn/ZnS-QDs) were synthesized at 120°C for 1 h. A 2 mL of 3000 mg L^{-1} Mn/ZnS-QDs modified with 300 µL of 1000 mg L^{-1} of NMPPy was selected to be a detecting reagent for the detection of methanol by digital-image colorimetry (DIC). Under the optimum conditions, the relationship between the ratio of red to green color intensity and the concentration of methanol standard solution was linear, with a linear range of 2%v/v to 50%v/v of methanol, with R-square of 0.9434 and a sensitivity of 3.569×10^{-3} $(\%v/v)^{-1}$, while the limit of detection (LOD) was reached at the concentration of 19.5%v/v. Additionally, a simple and inexpensive device has been created and tested for selectivity for methanol in comparison to a number of solvents. It was revealed that this device can be selective for methanol, providing the linearity of methanol detection in the range of 20%v/v to 80%v/v with R-square of 0.9918 and the sensitivity of 3.38×10^{-3} $(\%v/v)^{-1}$. According to the methanol detection in samples by DIC method from the different hand sanitizer gels, indicating that this device can be used to detect methanol in the hand sanitizer gel. Therefore, it can be concluded that this novel device was successfully used to examine samples of hand sanitizer gel with acceptable results.

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