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High Sensitivity Plasmonic Based on Triclopyr Butotyl Herbicide Sensor using Gold Nanorods (GNRs) as Sensing Material

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In this paper, we report the detection of triclopyr butotyl-based herbicide using a cost-effective and easy-to-use sensor offering fine-tuning of localized surface plasmon resonance (LSPR) responses. This sensor implements gold nanorods (GNRs) as its sensing material resulting in dual absorption bands corresponding to transverse surface plasmon resonance (t-SPR) and longitudinal surface plasmon resonance (l-SPR). The GNRs sensing material with an average length of 50 nm and surface density of ca.74% has been prepared using seed-mediated growth method through two-step processes; i.e., seeding and growth of the metallic nanocrystals. The sensing study was done by observing the change on peak intensity and position in different medium; D.I water and triclopyr butotyl solution. The results show these two sensing parameters were changed with the change of surrounding medium. Moreover, the LSPR sensor system was recorded to detect different concentrations of triclopyr butotyl from 3% to 32.1%.

Keywords: localized surface plasmon resonance; gold nanorods; optical sensor; triclopyr butotyl

I. INTRODUCTION

Gold nanoparticles (GNPs) present fascinating optical properties due to surface plasmons phenomenon resulting from collective oscillations of conduction band electrons in a metal, when the metal particle size approaches the electron mean free path length (~10 to 100 nm). Surface plasmon is depending on the size and shapes of metal nanoparticles. There are various shapes of GNPs that have been discovered such as octahedra (Cho *et al.*, 2010), rods (Lins *et al.*, 2017; Wang *et al.*, 2018; Nguyen *et al.*, 2016), plates (M. Morsin *et al.*, 2017), stars (Peter *et al.*, 2016), rices (Suratun *et al.*, 2018) and spherical (Nengsih *et al.*, 2012). The localized surface plasmon resonance (LSPR) in GNPs becomes important to control the structural, aspect ratios, shape and surrounding environment (M.Morsin *et al.*, 2012). Gold nanorods (GNRs) has a unique optical plasmon properties with dual intense of surface plasmon resonance peaks:(i) transverse surface plasmon resonance (t-SPR), and (ii) longitudinal surface plasmon resonance (l-SPR) peak. The transversal axis is tunable in lower wavelength region (visible) spectra, and the longitudinal axis is tunable in higher wavelength region (near-infrared) spectra. Due to high absorption intensity and fine-tuned wavelength on their longitudinal axis (l-SPR) over the visible to near-infrared region (Nguyen *et al.*, 2015; M.Morsin *et al.*, 2017), GNRs became a suitable candidate for LSPR sensing applications. Their sophisticated nanostructures have received interest and show great potential applications in biological imaging (Oza *et al.*, 2012), plasmonic sensing (M.Morsin *et al.*,

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2015), photothermal therapy (J. Sun *et al.*, 2014), and catalysis (Lu *et al.*, 2018).

For herbicide and pesticide sensing applications, there are several conventional methods used such as colourimetric (Priyadarshini *et al.*, 2017), electrochemical biosensor (D.Oliveira *et al.*, 2017) and fluorometric detection (Yue *et al.*, 2016). Colourimetric have been reported as cost-effective and facile methods for sensitive and selective detection of the pesticide in aqueous medium. The detection limit of colourimetric is at ~2.5 ppb (Jazayeri *et al.*, 2018). However, another pesticide detection method like electrochemical biosensor and fluorometric detection are portable device but not sufficiently sensitive towards surrounding medium changes. Furthermore, mostly detection of herbicide was done by using liquid chromatography tandem mass spectrometry (LC-MS/MS) (Stachniuk *et al.*, 2016), atmospheric pressure electrospray positive ionization LC-MS/MS (Thurman *et al.*, 2001) and gas chromatography (GC) system technique (Słowik-Borowiec *et al.*, 2015). These techniques present a good response, stability and sensitivity towards herbicide. In contrast of that technique, they require an expensive system setup, non-portable and complex procedure in the detection of herbicide. These problems motivate us for to explore a simple, easy-to-use and low-cost sensor system setup for detection of triclopyr butotyl.

This study reports a research on localized surface plasmon resonance (LSPR) sensor using GNRs as sensing material which optically response towards targeted analyte namely as triclopyr butotyl. Triclopyr butotyl ($C_{13}H_{16}Cl_3NO_4$) have been used to kill unwanted weeds, broadleaf plants, ants and control rust diseases in crops since 1979 (Dias *et al.*, 2017). Triclopyr butotyl is one of frequent herbicide used in agriculture especially for rice, barley and wheat farms. However, this light-brown liquid is toxic and unsafe for human either in long-term or short-term continuous exposure at low levels of herbicide usage. This herbicide was classified by the World Health Organization (WHO) as a moderately hazardous (Class II) active ingredients with CAS no.55335-06-3. Human is potentially exposed to triclopyr butotyl via ingestion of food containing residues that can produce toxic symptoms effect such as inhalation problem, vomiting and diarrhoea. Triclopyr butotyl was detected using optical response by injected triclopyr butotyl in growth solutions of GNRs which resulting high plasmonic sensitivity, fine-tunability and form a dual pair of plasmon bands.

II. MATERIALS AND METHOD

A. Materials

Five materials without any purification were used in this approach. They were sodium borohydride ($NaBH_4$, 98%), hexadecyltrimethylammonium bromide ($CTAB$, 99%), L-ascorbic acid (AA, 98%) and gold (III) chloride trihydrate ($HAuCl_4.\ 3H_2O$) products from Sigma Aldrich USA, and silver nitrate ($AgNO_3$) with purity 99.99% from Honeywell, Sigma Aldrich USA. All those materials must be dissolved in deionized water (D.I water). The substrates were cleaned with acetone, D.I water and 2-propanol to remove unwanted contaminants on the substrate surface.

B. Preparation of Gold Nanorods as Sensing Material

Gold nanorods (GNRs) were synthesized using a modified two-step approach by El-Sayed: (1) seeding process with 2 hours seed solutions ageing, and (2) growth of rod nanoparticles.

1. Seed Solutions Preparation

Cationic surfactant $CTAB$ of 15.0 mL, 0.60 M in micelles forms was mixed with 15.0 mL precursor reagent $HAuCl_4.\ 3H_2O$ with gentle stirring. The precursor agent reacts with $CTAB$ forms micelles in aqueous solutions to create a CTA^+-$AuCl_4^-$ complex. Freshly prepared 1.8 mL of ice-cold 0.01M $NaBH_4$, then injected into well-mix $CTAB$ and $HAuCl_4.\ 3H_2O$ solution. As a result, seed solution was produced in the form of a light brown solution. The presence of sodium borohydride reduces Au^{+3} ions to zero valent Au^0 to stabilize nanoseeds formation. After the solution was stirred for 1 min, it was kept undisturbed at room temperature for 2 h.

2. Growth Solutions Preparation

The aqueous solution of $CTAB$ 15 mL of 0.60M was added with 1.8 mL of 12 mM silver nitrate ($AgNO_3$) solution. In

sequence,15 mL of 3 mM $HAuCl_4.3H_2O$ precursor agent was mixed to this solution and then 0.21 mL of 0.24 M mild reducing agent L-ascorbic acid (AA) was added. This solution was mixed gently for 1 min at temperature of 25 °C, and the aqueous solution colour changes from yellowish to colourless. After the colour of solution changed, 45 µL of seed solution was injected and the growth solution was stirred vigorously for 1 min. Finally, the growth solution was kept for 20 h at room temperature. The growth solution turns to dark violet after 20 h overgrowth ageing procedure. The growth solution was centrifuged 3 times at 5000 rpm swing-out for 30 min and dispensed in 1 mL deionized water.

3. Characterization of Gold Nanorods (GNRs)

The optical absorption of the GNRs samples has been analysed by using Shimadzu UV-1800 UV/Visible Scanning Spectrophotometer, Japan with wavelength baseline ranges from 300 to 1000 nm by scanning dual spectral peaks which is transverse (t-SPR) and longitudinal surface plasmon resonance (l-SPR). Structural characterization of GNRs is obtained by using X-ray diffraction (XRD) from PANalytical Netherlands with CuKα radiation at the wavelength of 0.154 nm with a step size of 0.03°. The detected data is taken in a 2θ range from 20° to 80°. The morphology of nanostructures of the samples have been confirmed using field emission scanning electron microscope (FESEM), JEOL model JSM-7600F from the United States. The shape and dimension of GNRs were visualized at voltage 5 kV with magnification ranges from x10 000 to x150 000.

4. Plasmonic Sensor System Setup

Triclopyr butotyl was detected using an optical sensor to observe the optical response of gold nanorods (GNRs) towards that herbicide. Figure 1 presents the optical sensor system setup consists of cuvette holder, SE-P400-2-UV-SWIR fiber solarization-resistant optical fibers, DH2000-BAL balanced deuterium tungsten halogen light source, USB2000-UV-VIS spectrometer and computer with Ocean View software as a spectrum analyser. The cuvette holder is used as a place of sensing material and targeted analyte; i.e., GNRs solution and triclopyr butotyl. To perform sensitivity test, the cuvette holder will be filled by injecting 0.25 mL of deionized water in GNRs solution. Then, the surrounding medium was changed by replacing the D.I water with triclopyr butotyl. The light source provides illumination wavelength from 215 to 2000 nm was radiated in by one of optical fibre arm towards the GNRs sample. Then, the absorbed light was radiated out by the other optical fibre arm to the USB2000-UV-VIS spectrometer. The optical response of the GNRs was displayed on Ocean View software which shown the absorption spectra of GNRs solution and 10 % triclopyr butotyl. To observe the concentration effect of triclopyr butotyl, the solution was dissolved with 10 mL water with eight different concentrations at 3%, 5%, 10%, 15%, 20%, 25%, 30% and 32.1%. The response for each concentration was recorded. For example, 10% triclopyr butotyl was prepared by dissolving 4.524 mL triclopyr butotyl with 10 mL D.I water. The preparation for each concentration of triclopyr butotyl was done by referring Lorentz - Lorenz model (Kurt E. Oughstun et. al., 2003).

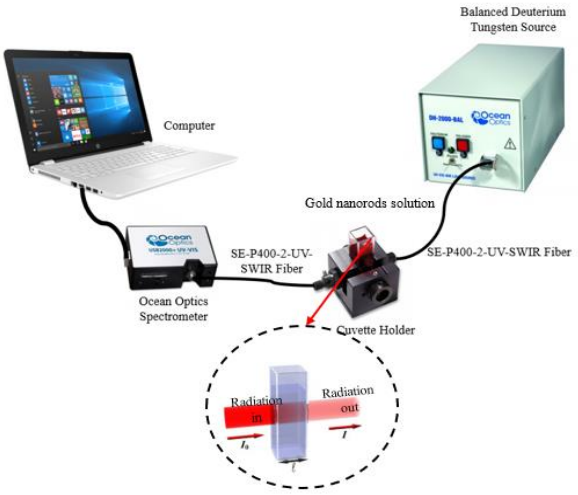

Figure 1. Optical sensor system to detect triclopyr butotyl herbicides

III. RESULTS AND DISCUSSION

A. Structural and Surface Morphology of GNRs as Sensing Material.

The X-ray diffraction (XRD) patterns of GNRs sensing material were obtained with Cu Ka source radiation at a

scanning rate of 2° min^{-1} from 20° to 80°. The XRD pattern of structural compositions on the surface sample is depicted in Figure 2. This sample shows crystallite structure with 3 dominated peaks, labelled as (h, k, l) index miller or crystallite's phases. The intensity of the (111) diffraction peak was strong at 38.147° that corresponds to crystallographic plane of face centered cubic (fcc) structure of metallic gold. The obtained data were matched well with Inorganic Crystal Structure Database (ICSD file no. 98-005-3763), which suggest the crystalline nature of gold nanostructure. The average crystallite size obtained is 216.31 Å which equals to 21.631 nm. The d-spacing for the sample is 2.35 Å which equals to 0.235 nm. The other diffraction peaks at [200] and [311] planes are weak and located at 44° and 77° respectively.

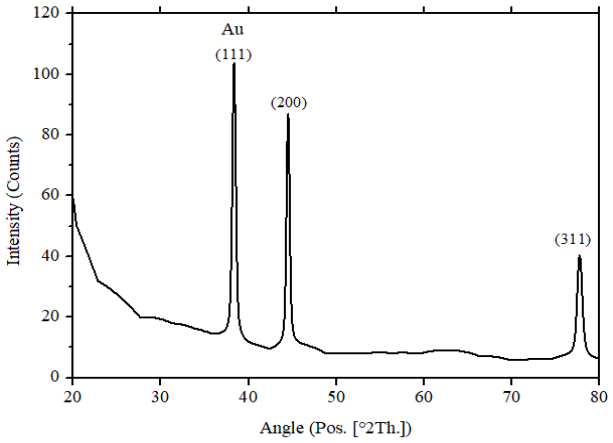

Figure 2. XRD pattern of structural compositions on the surface sample.

The GNRs morphological images were characterized using FESEM JEOL model JSM-7600F shown in Figure 3. Morphological images display the presence of 74% rods surface density with 45-55 nm length and 12-24 nm width. However, low yield of by-product nanoparticles was observed with estimated surface area around 19%. Medium size of GNRs is suitable for plasmonic sensing applications due to its sensitivity with surrounding medium changes (L. Feng et. al., 2015).

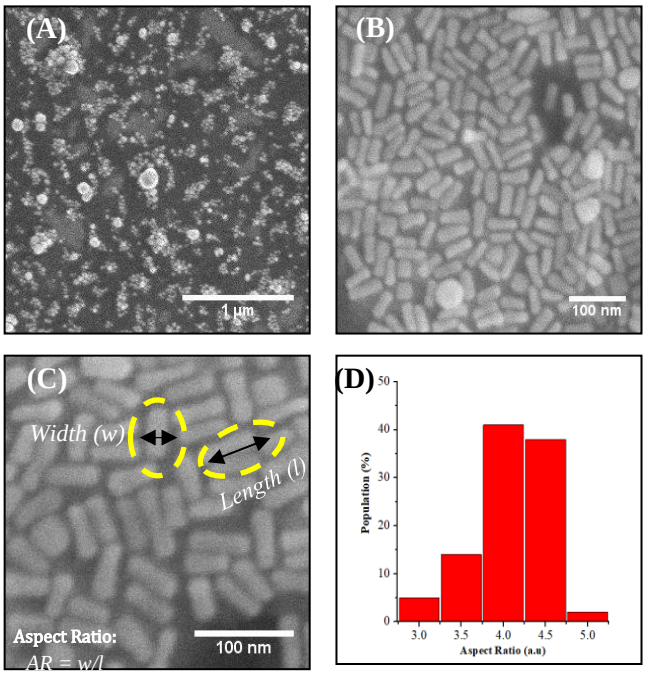

Figure 3. FESEM morphological images of the sample with different magnification resolution marked as; (A) x 10 000, (B) x 50 000, (C) x 100 000, (D) Population of GNRs aspect ratio

B. Sensitivity Measurement using Plasmonic Sensor.

The optical properties of the GNRs was studied in two different mediums; deionized (D.I) water and 10 % triclopyr butotyl ($C_{13}H_{16}Cl_3NO_4$) using our optical sensor system setup. The change of GNRs response towards different medium were recorded and shown in Figure 4. The tests were done in four (4) medium; A - GNRs only, B, GNRs with D.I water, C – GNRs with 10% triclopyr butotyl and D- 10% triclopyr butotyl only. All the responses with GNRs as sensing materials show two peaks corresponding to transverse surface plasmon resonance (t-SPR) and longitudinal surface plasmon resonance (l-SPR). Meanwhile, the sensor response in 10% triclopyr butotyl without GNRs shows no significant peaks of both l-SPR and t-SPR. Hence, the implementation of GNRs helps to increase the sensitivity of this sensor due to plasmonic effect as described in classical Mie theory [Purcell et. al., 1973].

Moreover, the optical spectra show that absorbance intensity and resonance peak position of localized surface plasmon resonance (LSPR) were changed when the D.I

water was added. Similar changes were also observed when the D.I water is replaced with 0.25 ml, 10% concentration of triclopyr butotyl solution in the GNRs solution. The change of the response can be related with the change in refractive indexes of surrounding medium: water (n=1.33) and triclopyr butotyl (n=1.59). The absorbance intensity of triclopyr butotyl at strong longitudinal plasmon resonance is 3.08, which is higher than water medium. For l-SPR, the absorption intensity gap between triclopyr butotyl and water is 6.18% while t-SPR shows a slight change. These results show that optical extinction spectrum of GNRs is sensitive towards refractive index sensitivity of the surrounding medium. Besides, it was observed that the change of l-SPR is larger than t-SPR. This is due to the GNRs aspect ratio. The longitudinal axis is more polarize and sensitive to aspect ratio changes (S. Lua et. al.,2018). The results are summarized in Table 1.

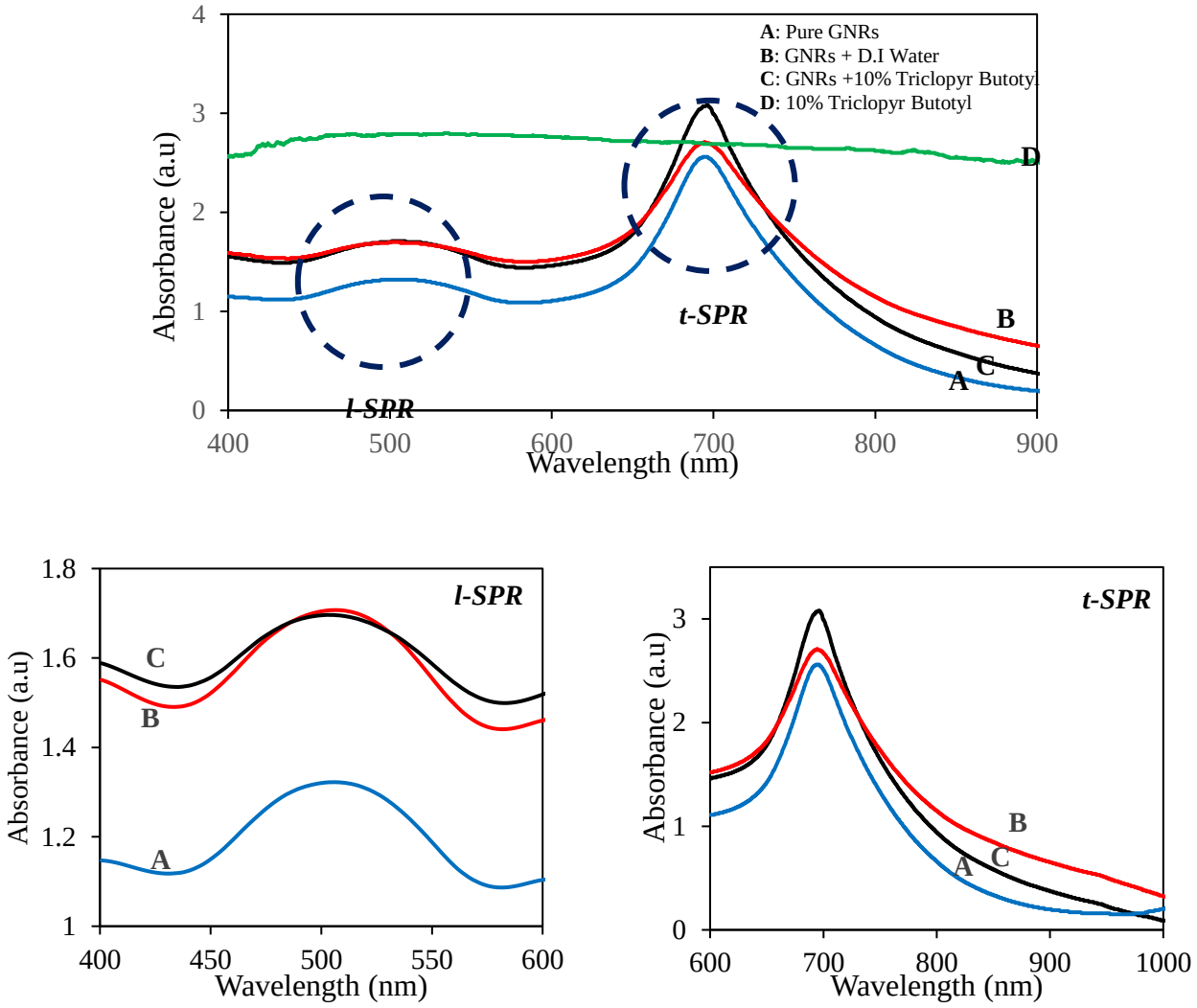

Figure 4. Optical responses spectra of GNRs in 3 different medium (A) Pure GNRs, (B) deionized water (GNRs + H_20), (C) 10% triclopyr butotyl (GNRs + $C_{13}H_{16}Cl_3NO_4$), and (D) 10% triclopyr butotyl ($C_{13}H_{16}Cl_3NO_4$)

Table 1. The transversal (*t-SPR*) and longitudinal (*l-SPR*) band peaks position of GNRs with three different mediums

Medium	***t-SPR* Δ peaks**		***l-SPR* Δ peaks**	
	λmax (nm)	Imax $(a.u)$	λmax (nm)	Imax $(a.u)$
Pure GNRs	502.97	1.32	693.48	2.56
GNRs + Water	504.26	1.71	694.29	2.71
GNRs + Triclopyr Butotyl	505.98	1.70	695.50	3.08

C. Plasmonic Response Towards Different Concentration of Triclopyr Butotyl- Based Herbicide Sensor

The peak position and absorbance intensity of the GNRs-based LPSR spectra in triclopyr butotyl solution were analysed to record its sensing sensitivity. The triclopyr butotyl solution were diluted with 10 mL deionized water for eight different concentrations; 3%, 5%, 10%, 15%, 20%, 25%, 30% and 32.1%. Figure 5 shows an optical response of triclopyr butotyl solution for different concentrations. From optical responses of t-SPR, it was found that the absorbance intensity of GNRs sample was linearly increased with the triclopyr butotyl concentrations of the herbicide. For l-SPR response, the absorbance intensity increases correspondingly from 2.86 a.u to 3.74 a.u and it was linearly increased with triclopyr butotyl concentration. For peak position change, as shown in Figure 5, the transversal and longitudinal resonance band are slightly changed when tested in different medium. When triclopyr butotyl concentrations reached 10% and more, the peak response remains in the wavelength of 739.88 nm. In this case, l-SPR is no longer shifting since binding of the analyte does not induce aggregation of GNRs.

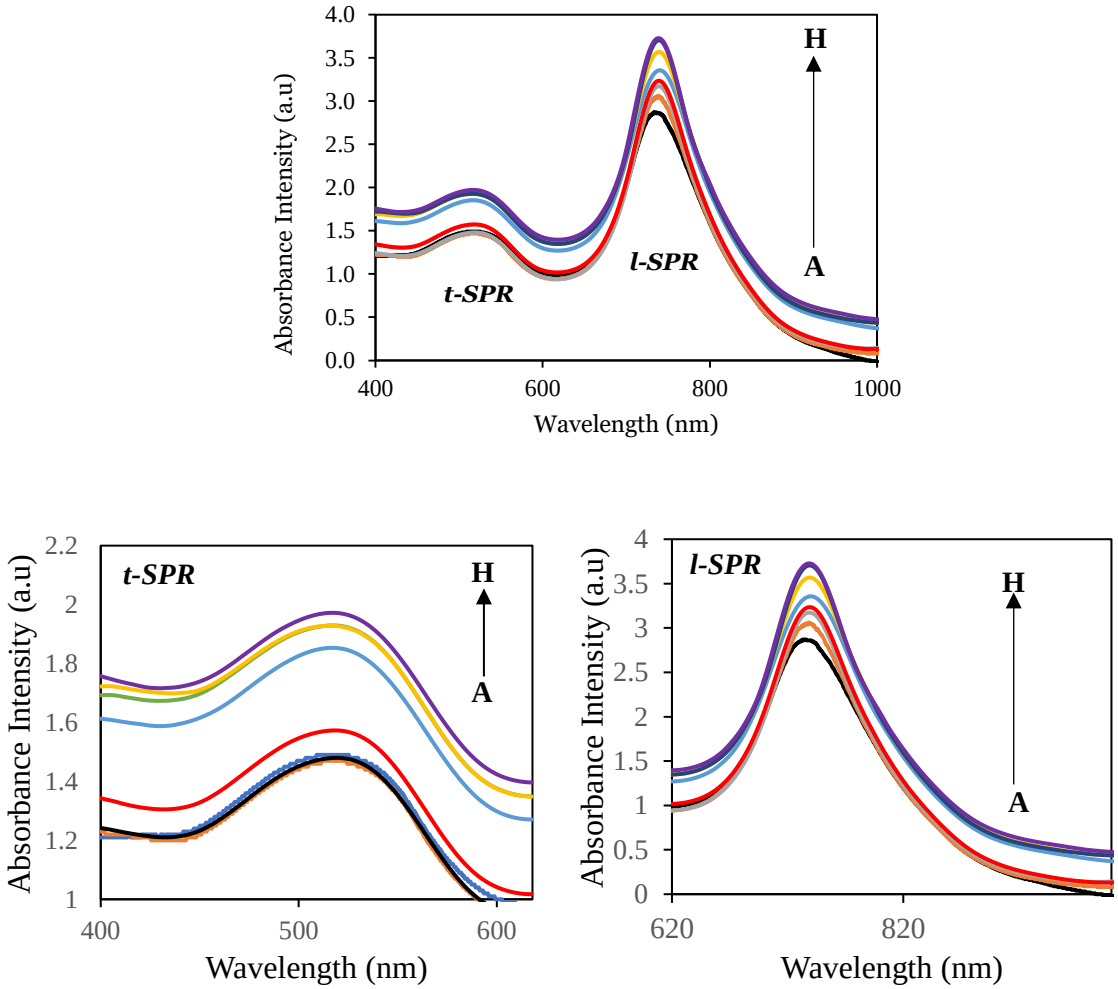

Figure 5. Absorption curves of t-SPR and l-SPR in response to triclopyr butotyl concentrations; (A) 3%, (B) 5%, (C) 10%, (D) 15%, (E) 20%, (F) 25%, (G) 30% and (H) 32.1%. Arrows show the trend in absorption spectra following increases in triclopyr butotyl concentration

IV. CONCLUSION

We successfully synthesis the medium size of gold nanorods (GNRs) using modified seed-mediated growth (SMG) technique to be used as sensing material in LSPR sensor. By using this technique, high homogeneity and fine-tuning of GNRs can be obtained with cost-effective synthesis procedure. The optical response of GNRs samples in air, deionized (D.I) water and triclopyr butotyl-based herbicides produced high sensitivity due to the absorbance intensities and peak position of these two absorption bands change linearly in change of surrounding medium. Besides, different concentrations of triclopyr butotyl as low as 3% can be detected by using developed optical LSPR sensor system. For future research, the selectivity of the sensor can be studied by modifying its sensing material with functionalized gold nanoparticles.

V. ACKNOWLEDGEMENT

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