# DEVELOPMENT OF PLASMONIC SENSOR USING GOLD NANOBIPYRAMIDS FOR DETECTION OF GLYPHOSATE BASED PESTICIDE

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A thesis submitted in
fulfillment of the requirement for the award of the
Doctor of Philosophy in Electrical Engineering

Faculty of Electrical and Electronic Engineering
Universiti Tun Hussein Onn Malaysia

FEBRUARY 2020

For my dearest family, supervisors, and friends.

**ACKNOWLEDGEMENT**

This thesis becomes a reality with the kind support and help of many individuals. I would like to extend my sincere thanks to all of them.

Foremost, I want to offer this endeavor to Allah, the Almighty, for the wisdom he bestowed upon me, the strength, peace of my mind and good health in order to finish my PhD research.

I would like to express my sincere gratitude to my supervisors, Dr. Marlia binti Morsin, Assoc. Prof. Dr. Nafarizal bin Nayan, and Dr. Nur Anida binti Jumadi for their continuous support, guidance, patience, motivation, and immense knowledge throughout the duration of this research. This work would not materialize without the financial support from UTHM under Research Grants and Contracts No. U565, W006, and H468.

My sincere thanks also go to Assoc. Prof. Dr. Mohd Zainizan bin Sahdan who give access to the Semiconductor Nanometerials Processing Research Laboratory, Mrs. Faezahana binti Mohkhter, and Mr. Ahmad Nasrull bin Mohamed for their technical support during the research.

My sense of gratitude also goes to my research lab colleagues and people who have willingly helped me out with their abilities.

Specially, my deepest appreciation belongs to my family for their patience and understanding.

# ABSTRACT

The development of plasmonic sensor using gold nanobipyramids (GNBPs) as sensing material for detection of glyphosate based pesticide (GBP) has been performed. The GNBPs was synthesised using seed-mediated growth method (SMGM). In the synthesis process, the effect of three different additive acid types which are chloric, sulfuric, and fluoric acid, and its concentration in growth solution were investigated to obtain optimum surface density and aspect ratio of GNBPs. The structure obtained is gold with face-centered cubic (FCC) crystal structure and diffraction peaks at $2\theta$ values of 38.2º and 44.5º, which corresponding to (111) and (200) planes, respectively. The GNBPs have surface density from 5.21±0.44 to 91.46±3.32% and aspect ratio from 2.00±0.02 to 2.76±0.05. It exhibits two resonance peaks at wavelength around 550 and 580 nm, corresponding to transverse surface plasmon resonance (t-SPR) and at wavelength around 720 and 780 nm, corresponding to longitudinal surface plasmon resonance (l-SPR). In sensing study, the changes in the peak position and intensity for both t-SPR and l-SPR, respectively, in de-ionized water (DIW) as reference and glyphosate solutions as target analyte were measured. The presence of glyphosate as low as 1 mg/mL was successfully detected using this sensor. Besides, gold bone nanorods (GBNRs) and gold nanorods (GNRs) have been employed as sensing material and the results show the GNBPs-based plasmonic sensor demonstrate improved sensitivity compared to other sensors. For t-SPR band, the GNBPs provided sensitivity factor as high as 4.76 and 5.17 times larger than the sensitivity factor of GBNRs and GNRs, while for l-SPR band, the sensitivity factor of GNBPs are 2.87 times larger than GBNRs and 1.57 times larger than GNRs. Also, the selectivity of GNBPs-based plasmonic sensor towards glyphosate is higher than its response to four different analytes, ie. chlorpyrifos, acetic acid and acetone. As a conclusion, the additive acid types and concentrations influenced the morphological of GNBPs and the implementation as a sensing

material in plasmonic sensor has been proven improved the sensitivity and has good selectivity towards glyphosate.

# ABSTRAK

Pembangunan sistem sensor menggunakan nanobipiramid emas (GNBPs) sebagai bahan penderia telah dibina bagi mengesan kehadiran racun perosak berasaskan glifosat (GBP). GNBPs telah berjaya ditumbuhkan menggunakan kaedah pertumbuhan berantara pembenihan (SMGM). Dalam proses sintesis, pengaruh tiga jenis asid penambah iaitu asid klorik, asid sulfurik, dan asid fluorik beserta kepekatannya dalam larutan penumbuh telah dikaji bagi mendapatkan ketumpatan dan aspek nisbah GNBPs yang optimum. Struktur yang dihasilkan adalah emas dengan struktur kristal kubus berpusat muka (FCC) dan puncak belauan pada kedudukan nilai 2θ 38.2º and 44.5º, yang masing-masing berpadanan dengan satah (111) dan (200). GNBPs yang terbentuk memiliki ketumpatan permukaan dari 5.21±0.44% hingga 91.46±3.32% dan aspek nisbah dari 2.00±0.02 hingga 2.76±0.05. Ianya mempunyai dua puncak resonan pada panjang gelombang sekitar 550 dan 580 nm, yang berpadanan dengan resonan plasmon permukaan melintang (t-SPR) dan pada panjang gelombang sekitar 720 nm dan 780 nm, berpadanan dengan resonans plasmon permukaan membujur (l-SPR). Dalam kajian penderiaan, perubahan kedudukan puncak dan perubahan keamatan puncak t-SPR dan l-SPR dalam air nyahion sebagai rujukan dan dalam larutan glifosat sebagai analit telah diukur. Kehadiran glifosat dengan kepekatan serendah 1 mg/mL telah berjaya dikesan menggunakan sensor ini. Selain itu, nanorod emas berbentuk tulang (GBNRs) dan nanorod emas (GNRs) telah digunakan sebagai bahan penderia dan hasilnya menunjukkan bahawa sensor plasmonik berasaskan GNBPs mempamerkan kepekaan yang lebih baik dibandingkan dengan sensor yang lain. Bagi puncak t-SPR, GNBPs memberikan kepekaan sebanyak 4.76 kali dan 5.17 kali lebih tinggi berbanding GBNRs dan GNRs. Manakala bagi puncak l-SPR, kepekaan GNBPs adalah 2.87 kali lebih tinggi daripada GBNRs dan 1.57 kali lebih tinggi daripada GNRs. Selanjutnya, kememilihan sensor berasaskan GNBPs terhadap glifosat adalah lebih tinggi daripada tindak balas sensor terhadap empat analit lain, iaitu klorpirifos, asid asetik

dan aseton. Sebagai kesimpulan, jenis asid penambah dan kepekatannya berpengaruh terhadap morfologi GNBPs dan penggunaan GNBPs sebagai bahan penderia dalam sensor plasmonik telah terbukti meningkatkan kepekaan dan kememilihan yang baik dalam mengesan kehadiran glifosat.

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# LIST OF SYMBOLS AND ABBREVIATIONS

| | | |
|---|---|---|
| 2θ | - | Angle of X-ray diffraction |
| Ǻ | - | Amstrong |
| ºC | - | Degree Celsius |
| ° | - | Degree |
| % | - | Percent |
| ε | - | Dielectric constant |
| µg | - | Microgram |
| a.u | - | Arbitrate unit |
| Ag | - | Silver |
| AR | - | Aspect ratio |
| Au | - | Gold |
| $CH_2COOH$ | - | Acetic acid |
| $CH_2O$ | - | Formaldehyde |
| $CH_3OH$ | - | Methanol |
| $CH_4$ | - | Hydrocarbon |
| $Cl_2$ | - | Chlorin |
| $ClCH_2COOH$ | - | Chloroacetic acid |
| CoR | - | Coefficient of repeatability |
| CTAB | - | Cetyltrimethylammonium bromide |
| CTAC | - | Cetyltrimethylammonium chloride |
| CTBAB | - | Cetyltributhylammonium bromide |
| CTEAB | - | Cetyltriethylammonium bromide |
| Cu | - | Copper |
| DDA | - | Discrete dipole approximation |
| DEA | - | Diethanolamine |
| DIW | - | De-ionized water |
| DMPP | - | Dimethyl phosphonate |

| | | |
|---|---|---|
| DSIDA | - | Disodium iminodiacetic acid |
| E | - | Electric field |
| EFSA | - | European food safety authority |
| ELISA | - | Enzyme-linked immunosorbent assay |
| FCC | - | Face-centered cubic |
| Fe | - | Ferrum |
| FESEM | - | Field emission scanning electron microscopy |
| FFT | - | Fast fourier transform |
| FOM | - | Figure of merit |
| FWHM | - | Full width at half maximum |
| GBNRs | - | Gold bone nanorods |
| GBP | - | Glyphosate based pesticide |
| GC | - | Gas chromatography |
| GNBPs | - | Gold nanobipyramids |
| GNPls | - | Gold nanoplates |
| GNPs | - | Gold nanoparticles |
| GNRs | - | Gold nanorods |
| GNSs | - | Gold nanosphericals |
| GNTs | - | Gold nanotriangles |
| HCl | - | Hydrochloric acid |
| HCN | - | Hydrocyanic acid |
| HPLC | - | High-performance liquid chromatography |
| IARC | - | International agency for research on cancer |
| ICSD | - | Inorganic crystal structure database |
| IDAN | - | Iminodiacetonitrile |
| ITO | - | Indium tin oxide |
| IUPAC | - | International union of pure and applied chemistry |
| K | - | Kelvin temperature |
| kV | - | Kilo volt |
| L | - | Liter |
| $LC_{50}$ | - | Lethal concentration |
| $LD_{50}$ | - | Lethal dose |
| LoD | - | Limit of detection |
| LSPR | - | Localized surface plasmon resonance |

| | | |
|---|---|---|
| l-SPR | - | Longitudinal surface plasmon resonance |
| nm | - | Nanometer |
| *m* | - | Sensitivity factor |
| M | - | Molarity |
| mA | - | Mili ampere |
| MEA | - | Monoethanolamine |
| mg | - | Miligram |
| mL | - | Mililiter |
| MLWA | - | Modified long wavelength approximation |
| mM | - | Milimolar |
| MNPs | - | Metal nanoparticles |
| *n* | - | Refractive index |
| NaOH | - | Sodium hydroxide |
| $NEt_3$ | - | Triethylamine |
| $NH_3$ | - | Ammonia |
| $PCl_3$ | - | phosphorus chloride |
| Pd | - | Palladium |
| pKa | - | Acidity constant |
| PMIDA | - | N-phosphonomethyliminodiacetic acid |
| Pt | - | Platinum |
| $R^2$ | - | Correlation coefficient |
| RIS | - | Refractive index sensitivity |
| RIU | - | Refractive index unit |
| RPM | - | Radians per minute |
| SERS | - | Surface enhanced Raman scattering |
| SMGM | - | Seed-mediated growth method |
| TLC | - | Thin-layer chromatography |
| t-SPR | - | Transverse surface plasmon resonance |
| USA | - | United States of America |
| UV-Vis | - | Ultraviolet-visible |
| WHO | - | World health organization |
| XRD | - | X-ray diffraction |

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# LIST OF PUBLICATIONS

**Journals:**

(i) **Suratun Nafisah**, Marlia Morsin, Nur Anida Jumadi, Nafarizal Nayan, Nor Shahida Mohd Shah, Nur Liyana Razali, Nur Zehan An'Nisa (2020) "Improved sensitivity and selectivity of direct localized surface plasmon resonance sensor using gold nanobipyramids for glyphosate detection." IEEE Sensors Journal. Vol. 20, No. 5, pp. 2378-2389.

(ii) **Suratun Nafisah**, Marlia Morsin, Nur Anida Jumadi, Nafarizal Nayan, Nur Liyana Razali, Nur Zehan An'Nisa Md Shah (2018) "One-step wet chemical synthesis of gold nanoplates on solid substrate using poly-l-lysine as reducing agent." MethodsX. Vol. 5, pp. 1618-1625.

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