UNIVERSITI MALAYSIA PERLIS
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International Journal of Nanoelectronics and Materials
IJNeaM
ISSN 1985-5761 | E-ISSN 2232-1535

Amperometric identification of metronidazole in urine by Au-Pd core-shell nanoparticles dispersed in Laponite clay/glassy carbon electrode

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Received 09 October 2025, Revised 15 October 2025, Accepted 29 October 2025

ABSTRACT

A colloidal suspension of Au-Pd nanocluster-dispersed laponite was synthesized by a single-step reduction of equimolar concentrations of $HAuCl_4$ and K_2PdCl_4 in the presence of laponite using ascorbic acid. UV-visible spectroscopy and SEM studies proved the formation of bimetallic core-shell Au-Pd on the laponite clay matrix. The metronidazole's electrochemical behaviour was analyzed with bimetallic nanoparticles dispersed in a laponite composite modified glassy carbon electrode (GCE). An irreversible reduction peak was noted in cyclic voltammetry at +0.80 V vs. Ag/AgCl. Detection of metronidazole antibiotic drug at lower level in biological samples was analyzed by amperometric method and pulse voltammetry. A linear regression was achieved in the range between 0.5 and 10 µM in both methods. The present can be extended further to use for the sensitive and selective electrochemical detection of metronidazole in real urine samples.

Keywords: *Antibiotic drug, Laponite, Electrocatalytic reduction, Alloy nanoparticles*

1. INTRODUCTION

Laponite is a nanoscale disc-shaped platelet, which contains hydrous sodium lithium magnesium silicate with less than diameter of 25 nm and thickness of 1 nm. Because of the unique anisotropic interactions between the nanoplates caused by the positive and negative charges on the clay facets and nanosilicate edge, nanosilicates can interact with small molecules, enzymes, and anionic, cationic, and neutral polymers [1]. Individual platelets released sodium ions when laponite clay was dissolved in water, leaving each platelet's faces negatively charged with hydroxide ions and its edges slightly positively charged. Laponite colloidal crystals form a gel-like structure because of their charge distribution on laponite nanoplatelets and their capacity to form a stable arrangement. It can be used as solid support to immobilise metal nanoparticles for various catalytic applications because of high thermal stability and gelation behaviour [2–4]. Because of its chemical inertness and low toxicity, it can be used as nanocarrier as well as dispersing agent in drug-delivery and health care products [5–7]. It has been reported that numerous brilliant-coloured dyes can intercalate within laponite by intercalation to form highly stable pigments, called, 'Maya Blue', which were employed for painting in ancient days [8]. Colloidal dispersion of laponite clay can be used to stabilize enzyme substrates to facilitate direct electron transfer catalytic reactions, therefore, resulting composite can be used to fabricate biosensors for sensing glucose and phenol [9, 10].

In contrast to their monometallic counterparts, bimetallic core-shell nanocrystals (NCs) are a new and significant family of material with unique characteristics for the efficient control of optical and electrical properties. For example, core-shell NCs based on Pt, Pd, and Au that are sized and shaped precisely offer advantageous optical and catalytic qualities [11]. Recently, bimetallic nanomaterials have attracted growing interest because of their inherent advantages, like chemical reactivity, stability and selectivity. Among different bimetallic systems, Au–Pd bimetallic nanoparticles are having promising catalytic systems, make them significant candidates for catalytic degradation of chloroorganic pollutants [12], ethanol oxidation [13] and photochemical hydrogen generation [14]. Recent research has shown that combining graphene sheets with bimetallic nanocomposites greatly enhances the electron transfer and electrocatalytic properties of the nanocomposites. The nanocomposites of Au-Pd/rGO/GCE have higher conductivity with excellent catalytic properties, which confirms the simultaneous determination of CC, HQ, and RC [15]. Similarly, bimetallic nanomaterial-coated electrodes were utilized for the simultaneous identification glucose, hydrogen peroxide [16], hydrazine [17], and sensing biological molecules and drugs [18, 19]. Recently, bimetallic nanoparticles supported by laponite clay have been demonstrated by utilizing the reducing agent of ascorbic acid. The resulting bimetallic nanoparticles dispersed in laponite gels have been used as catalyst for reduction of 4-nitrophenol with enhanced catalytic activity [20]. A limited application has been reported in the literature on the electrocatalytic behaviour of metal nanoparticles dispersed in laponite clay gel so far. Therefore, authors want to exploit the use of nanocomposites consisting of Au-Pd core-shell nanoparticles based on laponite disc-shaped clay as solid support, a promising candidate for electrochemical sensor applications. Metronidazole is a simple nitroimidazole-functionalised antibiotic drug, and it is a routinely used antibacterial, antiprotozoal and anti-inflammatory drug [21, 22]. It can be used to cure various diseases, including parasitic and respiratory infectious diseases like coronavirus. Long-term consumption of the MTZ caused rigorous health hazards to human beings because of its genotoxicity and mutagenetic-based side effects [23]. By considering the toxicity and adverse effects, there is a demand to develop a new methodology to determine its concentration in biological samples accurately. Many techniques identified for quantitative sensing of metronidazole in biological samples, such as UV-visible spectrophotometry [24], spectrofluorimetry [25], and HPLC [26]. In general, all these techniques are expensive, and need skilled operators to perform experiments and the pretreatment process. To circumvent all these obstacles, this study uses electrochemical techniques to detect molecule at trace level. Electrochemical techniques like differential pulse voltammetry (DPV) and amperometry methods are prone analytical tools for the identification of drugs in real-life samples.

In the present, the metronidazole antibiotic, a nitro group, is a functional drug molecule that was chosen, which undergoes a reduction reaction, and it is favourable for the cathodic reduction process without much interference from oxidation processes arising from bioactive molecules present in biological samples. Nevertheless, electrode fouling and poor electrochemical response during the reduction process are some of the inevitable problems. To overcome these issues, we preferred to modify the electrode surface with various polymer films and redox mediators to eliminate electrode fouling and enhance electrocatalysis, the sluggish electron transfer process [27]. Comprehensive reviews have been reported in the literature on the detection of metronidazole using numerous nanomaterial-modified electrodes [28–30]. Among all those modified electrodes, Ni-Fe LDH [31], Ni-Co LDH on CNF [32], 3D carbon/polythionine [33], Ag@PDDA/rGO [34], AgNP-Gr [35], Al_2O_3 hollow sphere [36], Chit-TsCuPc [37], PDA/CNT [38], and PtNP/polyfurfural modified electrode [39] have shown an outstanding electrochemical method of identification of metronidazole. In this current work, we are interested in exploiting the possibility of using Au-Pd bimetallic core-shell nanoparticles dispersed in laponite for electrochemical detection of MTZ in biological samples.

2. EXPERIMENTAL SECTION

2.1. Chemicals

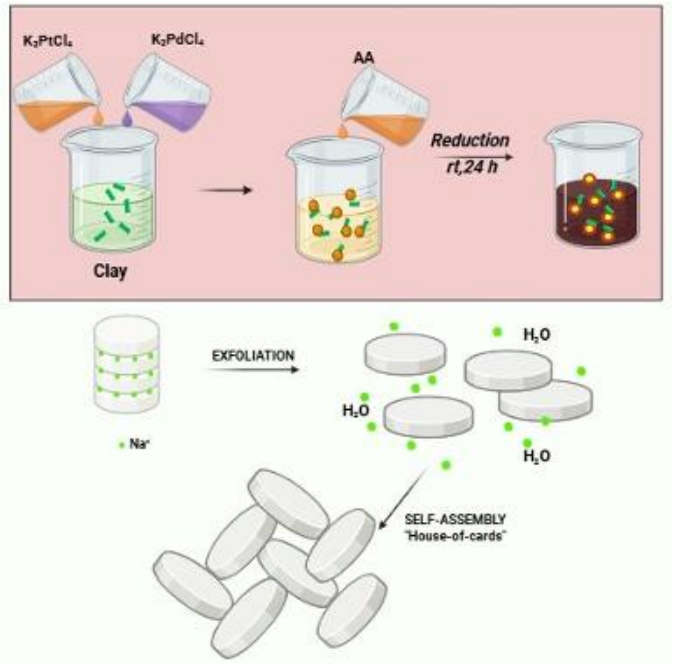
All chemicals are bought from commercial sources. The metal salts like $HAuCl_4 \cdot 2H_2O$ and K_2PdCl_4 were purchased from Sigma-Aldrich Chemicals, Bicorporal Corporation, Bangalore, India. Metronidazole was purchased from TCI Chemicals, India. Laponite® RD clay was obtained from Talas, NY, USA.

2.2. Instruments

A Shimadzu UV-visible spectrophotometer from Japan was used to record the UV-visible spectrum. With the use of FESEM (JEOL-JSM-6360, USA), the structural characteristics of nanomaterials were examined. A CHI 660A electrochemical apparatus, manufactured in the USA, was utilized to conduct the cyclic voltammetry. Ag/AgCl, platinum wire, and a glassy carbon electrode were utilized as counter electrodes in a three-electrode system with a single-compartment quartz cell that was purchased from BAS. Pvt. Ltd., USA. The ideal parameters for the DPV experiment were a 50 mV pulse amplitude, a 0.05 s pulse width, and a 0.2 s of pulse period. For amperometry studies, the reduction potential was set at +0.7 V vs. Ag/AgCl, and the experiment was carried out under constant stirring of electrolyte solution of pH 7.0.

2.3. Synthesis of Au-PdNC/Laponite

We have synthesised Au-Pd NC/Laponite (Scheme 1) based on the previous literature's reported procedure [20]. In short, 1 ml of 20 mM of $HAuCl_4 \cdot 2H_2O$ (20 mM) and 1 mL of 20 mM of K_2PdCl_4 were thoroughly combined with clay



Scheme 1. *In situ* synthesis of Au-Pd nanoclusters dispersed in laponite using ascorbic acid as a reducing agent

dispersion (1 mL; 2 wt%) in a glass vial of 5 ml to create Au–Pd core–shell NCs. After that, 0.5 ml of 0.4 M ascorbic acid was rapidly injected into the vial while being sonicated for 10 minutes at room temperature. After that, the reaction mixture was left to remain overnight, and then the solid nanoparticle was isolated by centrifugation for 10 min. The product further underwent two DI water washes before being dried in a nitrogen atmosphere.

3. RESULTS AND DISCUSSION

It has been reported that laponite can be used as solid support to immobilise Au-Pd core-shell nanoparticles by using ascorbic acid, as reported recently. The Au-Pd core-shell nanoparticle formation was confirmed by UV-visible spectroscopy and SEM studies. The occurrence of gold nanoparticles was seen at 520 nm, whereas the plasmon band became flat after the addition of palladium nanoparticles. Due to the emergence of Au-Pd core-shell nanoparticles, the plasmon band for AuNP disappeared, and the dampening of the SPR confirmed the existence of Au-Pd core-shell nanoparticles.

3.1. SEM Studies

SEM images of the Au-Pd nanoparticles dispersed in laponite gel are shown in Figure 1. The solid particles were seen from SEM images. The distribution of the nanoparticles within the laponite gel matrix can be monitored by SEM studies that show white spots. The loading of the core-shell form of Au-Pd nanoparticles was confirmed from EDX analysis.

3.2. Electrochemical Oxidation of Metronidazole at Au-Pd/Laponite Gel

The bimetallic Au-PdNPs have been used for the catalytic reduction of 4-nitrophenol recently [20]. We have used the bimetallic Au-PdNP core-shell nanoparticles scattered in a laponite gel-modified electrode for the electrochemical detection of metronidazole due to its large surface area and catalytic activity. Using cyclic voltammetry in 0.1 M PB solution with KCl as a supporting electrolyte, the electrocatalytic behaviour of MTZ at Au-Pd dispersed laponite-modified GCE was investigated (Figure 2). Without significantly changing its reduction peak potential of −0.8 V vs. Ag/AgCl, a higher reduction current was observed at the bimetallic nanoparticle-modified GCE in comparison to the naked GCE. The electrocatalytic reduction of metronidazole in phosphate buffer medium at modified GCE is shown schematically in the inset.

The calibration plot for the rise in current as a function of metronidazole concentration using Au-PdNP/laponite-modified GCE is displayed in Figure 3. The current rose linearly as the metronidazole concentration rose, and a repeatable current response was observed when the MTX concentration rose linearly. It was identified that the Au-Pd core-shell nanoparticles dispersed in laponite exhibit a significant increase in current response, indicative of the greatly improved catalytic activity (Figure 3). The influence of potential scan rate on electrocatalytic reduction of metronidazole was carried out to understand whether the reduction of metronidazole is diffusion controlled or adsorption controlled. A linear graph was created by plotting the square root of the scan rate against the peak current by the cyclic voltammetry method under optimised experimental conditions. Therefore, it is evidenced that the reduction of metronidazole at Au-Pd NPs Laponite gel-modified GCE is a diffusion-controlled reduction process.

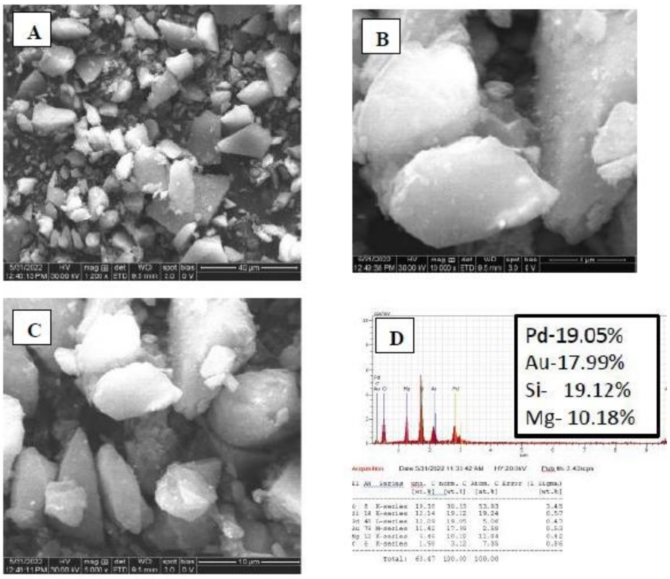


Figure 1. SEM images of Au-Pd core-shell nanoparticles dispersed in Laponite. Different magnifications of Au-Pd core-shell dispersed in Laponite (A), (B), and (C) and EDX pattern with chemical composition (D)

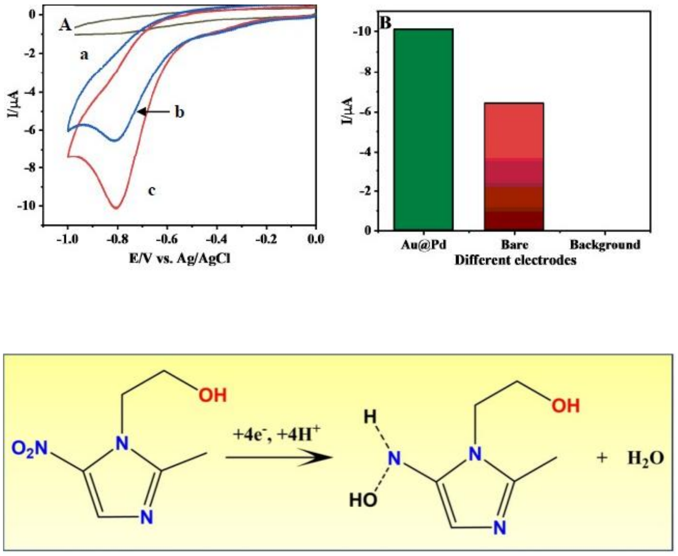


Figure 2. Cyclic voltammograms of bare GCE (a), MTZ (0.1 mM) at GCE (b), and Pd@Au/ Laponite-modified GCE in the presence of MTZ (c) at a scan rate of 50 mV·s⁻¹ (A) and (B).
Lower panel: The electrocatalytic reduction of metronidazole in phosphate buffer medium at modified GCE

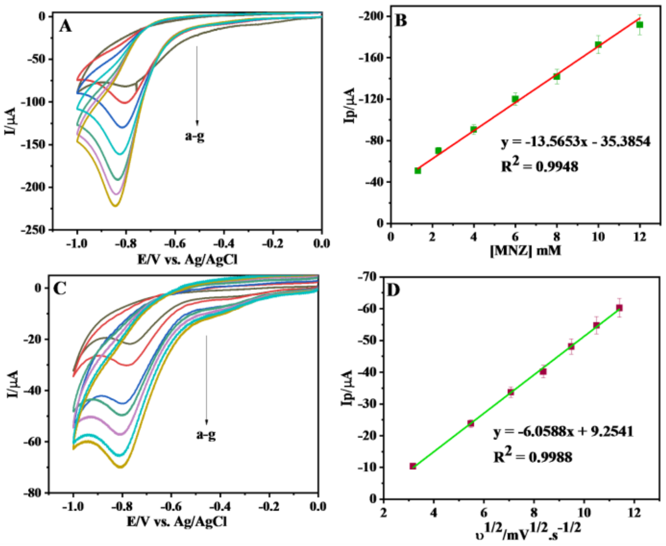


Figure 3. Cyclic voltammograms of MTZ on Pd@Au/Laponite/GCE at different concentrations from 11.1 × 10^{-3} M to 6.0 × 10^{-5} at a scan rate 50 mV·s^{-1} (A). Linear calibration plot of conc. vs. peak current of CV curves of (A) in (B). Cyclic voltammogram of MTZ (3.3 × 10^{-4} M) at Au-Pd NP Laponite/GCE at different scan rates ranging from 10 to 300 mV·s^{-1} (C) and linear relationship between Ip vs. scan rate (D)

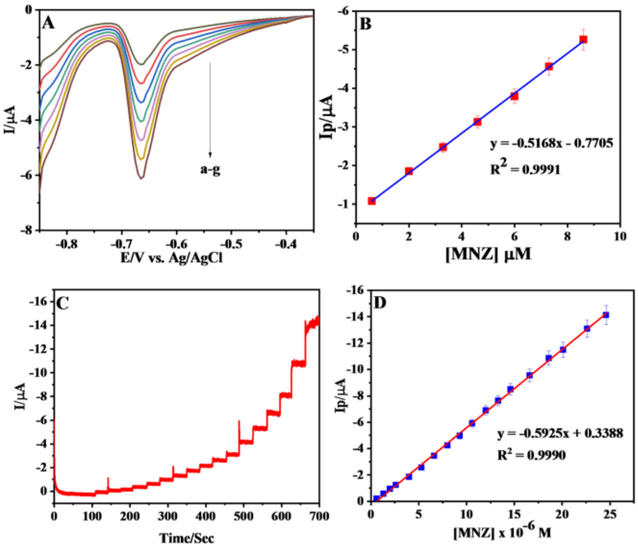


Figure 4. Differential pulse voltammetry response of MTZ at Au-Pd NP Laponite/GCE (0.5 μM to 9.0 μM) (A) and its calibration plot is shown in B. Amperometric response for metronidazole for each increment and its calibration plot (C and D)

3.3. Electrochemical Determination of Metronidazole

For quantification of metronidazole, the differential pulse voltammetry method was utilized on the modified electrode to lower the detection limit. A well-defined differential voltammogram was seen with a peak at −0.67 V vs. Ag/AgCl. The DPV responses at varying concentrations of metronidazole in micromolar concentration ranges are shown in Figure 4.

By this method we can determine the concentration of metronidazole in submicromolar ranges. On the other hand, the amperometry response on electrocatalytic reduction of metronidazole was investigated by measuring the rise in peak current while increasing the addition of metronidazole at a fixed potential of −0.70 V vs. Ag/AgCl under constant stirring (Figure 4). The linear graph was drawn by plotting the concentration of metronidazole with respect to the amperometric current response. The detection limit was obtained from the calibration plot. From this it is possible to estimate the concentration of 50 nM of metronidazole based on Au-Pd bimetallic nanoparticles in laponite gel modified GCE.

3.4. Real Sample Analysis

The present modified electrode of Au-Pd/Laponite-modified GCE was employed for sensing of antibiotic drug presence in urine samples. Samples were collected and stored at 5°C until further use. Determining the concentrations of MTZ present in the urine sample was carried out under optimised experimental conditions. About 5 mL of urine samples was taken and then diluted with DI water to make up to 25 mL volume standard flasks. Urine samples were treated with a known quantity of MTZ, which was sub Following appropriate dilution with buffer solution and in the presence of supporting electrolyte, a known quantity of MTZ was administered to the urine samples and subsequently measured. Following the recording of DPV, the calibration graph was used to calculate the unknown concentration of MTZ. Table 1 shows the anticipated outcomes of the sensor modified with Au-Pd alloy laponite gel. The stock solution, which had final concentrations of 85, 95, 110, and 125 μM in diluted urine samples, was mixed with a known quantity of MTZ to create the MTZ-spiked real sample solutions. MTZ recovery from urine samples that had been tampered with was computed three times, and the average results were tabulated [37]. Urine samples were treated with a known quantity of MTZ, which was sub Less than 3.5% was the relative standard deviation (n = 5). The suggested method can be used to measure the MTZ concentration level in a variety of clinical samples since it allows for a more precise and accurate inference of MTZ recovery in biological samples based on experimental performance.

We have tested DPV and amperometry for determining sensitivity and detection limit. DPV method is more sensitive and eliminates all residual and charging currents. Using this technique we only measured the faraday currents, on the other hand, the amperometry technique can be employed for sensing real samples. This experiment was carried out under stirring condition, therefore, the

Table 1. Determination of Metronidazole in urine samples (n = 5)

Urine samples	Spiking MTZ (μM)	Found (μM)	RSD (%)	Recovery (%)
1	5	4.95	3.2	99.0
2	10	9.80	2.1	98.0
3	15	14.90	3.7	99.0
4	20	20.01	3.6	100.5
5	25	24.80	4.2	99.0

measured current is purely due to reduction reaction i.e. reduction in current. Besides, electrode fouling was eliminated by this method.

4. CONCLUSION

In summary, we have developed an Au@Pd/Laponite nanocomposite, which we have successfully synthesised chemically and modified on GCE, for the sensitive determination of metronidazole in urine samples. The synthesised nanocomposite was successfully characterised with UV-visible, DLS and SEM studies. The electrochemical sensing behaviour of metronidazole with the bare GCE and Au@Pd/Laponite/GCE was monitored by using cyclic voltammetry. The nanocomposite-modified GCE can be used for sensing metronidazole, and it is inferred that the proposed method can be extended for sensing metronidazole with good sensitivity.

ACKNOWLEDGMENTS

The authors are grateful to Prof. Muthusamy Thangaraju, Augusta University, USA for provide laponite sample as gift sample.

REFERENCES

[1] P. A. Wheeler, J. Wang, J. Baker, and L. J. Mathias, “Synthesis and Characterization of Covalently Functionalized Laponite Clay,” *Chemistry of Materials*, vol. 17, no. 11, pp. 3012–3018, 2005.

[2] N. Aihara, K. Torigoe, and K. Esumi, “Preparation and Characterization of Gold and Silver Nanoparticles in Layered Laponite Suspensions,” *Langmuir*, vol. 14, no. 17, pp. 4945–4949, 1998.

[3] K. Haraguchi and D. Varade, “Platinum–polymer–clay nanocomposite hydrogels via exfoliated clay-mediated in situ reduction,” *Polymer*, vol. 55, no. 10, pp. 2496–2500, 2014.

[4] E. H. Hill, N. Claes, S. Bals, and L. M. Liz-Marzán, “Layered Silicate Clays as Templates for Anisotropic Gold Nanoparticle Growth,” *Chemistry of Materials*, vol. 28, no. 14, pp. 5131–5139, 2016.

[5] S. Wang *et al.*, “Laponite Nanodisks as an Efficient Platform for Doxorubicin Delivery to Cancer Cells,” *Langmuir*, vol. 29, no. 16, pp. 5030–5036, 2013.

[6] J. Onojah, W. Gebrehiwot, and D. Raghavan, “Advances of LAPONITE®-based nanocarrier in drug delivery applications,” *Biomaterials Science*, vol. 13, no. 18, pp. 4858–4884, 2025.

[7] K. S. Katti, H. Jasuja, S. v. Jaswandkar, S. Mohanty, and D. R. Katti, “Nanoclays in medicine: a new frontier of an ancient medical practice,” *Materials Advances*, vol. 3, no. 20, pp. 7484–7500, 2022.

[8] M. M. Lezhnina, T. Grewe, H. Stoehr, and U. Kynast, “Laponite Blue: Dissolving the Insoluble,” *Angewandte Chemie International Edition*, vol. 51, no. 42, pp. 10652–10655, 2012.

[9] D. Shan, J. Zhang, H.-G. Xue, S.-N. Ding, and S. Cosnier, “Colloidal laponite nanoparticles: Extended application in direct electrochemistry of glucose oxidase and reagentless glucose biosensing,” *Biosensors and Bioelectronics*, vol. 25, no. 6, pp. 1427–1433, 2010.

[10] Q. Fan, D. Shan, H. Xue, Y. He, and S. Cosnier, “Amperometric phenol biosensor based on laponite clay–chitosan nanocomposite matrix,” *Biosensors and Bioelectronics*, vol. 22, no. 6, pp. 816–821, 2007.

[11] H. Lin *et al.*, “Bimetallic nanoparticles: advances in fundamental investigations and catalytic applications,” *Environmental Science: Advances*, vol. 4, no. 1, pp. 33–56, 2025.

[12] M. O. Nutt, J. B. Hughes, and M. S. Wong, “Designing Pd-on-Au Bimetallic Nanoparticle Catalysts for Trichloroethene Hydrodechlorination,” *Environmental Science & Technology*, vol. 39, no. 5, pp. 1346–1353, 2005.

[13] L. S. R. Silva *et al.*, “AuPd/C core–shell and alloy nanoparticles with enhanced catalytic activity toward the electro-oxidation of ethanol in alkaline media,” *Applied Catalysis B: Environmental*, vol. 251, pp. 313–325, Aug. 2019.

[14] H. Rajashekhar *et al.*, “Bimetallic AuPd alloy nanoparticles on TiO_2 nanotube arrays: a highly efficient photocatalyst for hydrogen generation,” *Nanotechnology*, vol. 36, no. 20, p. 205401, 2025.

[15] Y. Chen *et al.*, “Ultrasensitive and simultaneous detection of hydroquinone, catechol and resorcinol based on the electrochemical co-reduction prepared Au-Pd nanoflower/reduced graphene oxide nanocomposite,” *Electrochimica Acta*, vol. 231, pp. 677–685, 2017.

[16] X. Li and X. Du, “Molybdenum disulfide nanosheets supported Au-Pd bimetallic nanoparticles for non-enzymatic electrochemical sensing of hydrogen peroxide and glucose,” *Sensors and Actuators B: Chemical*, vol. 239, pp. 536–543, 2017.

[17] P. B. Deroco, I. G. Melo, L. S. R. Silva, K. I. B. Eguiluz, G. R. Salazar-Banda, and O. Fatibello-Filho, “Carbon black supported Au–Pd core-shell nanoparticles within a dihexadecylphosphate film for the development of hydrazine electrochemical sensor,” *Sensors and Actuators B: Chemical*, vol. 256, pp. 535–542, 2018.

[18] J. Jiang and X. Du, “Sensitive electrochemical sensors for simultaneous determination of ascorbic acid, dopamine, and uric acid based on Au@Pd-reduced graphene oxide nanocomposites,” *Nanoscale*, vol. 6, no. 19, pp. 11303–11309, 2014.

[19] B. Hatamluyi, F. Lorestani, and Z. Es’haghi, “Au/Pd@rGO nanocomposite decorated with poly (L-Cysteine) as a probe for simultaneous sensitive electrochemical determination of anticancer drugs, Ifosfamide and Etoposide,” *Biosensors and Bioelectronics*, vol. 120, pp. 22–29, 2018.

[20] D. Varade and K. Haraguchi, “Novel bimetallic core–shell nanocrystal–clay composites with superior catalytic activities,” *Chemical Communications*, vol. 50, no. 23, pp. 3014–3017, 2014.

[21] N. Dione, S. Khelaifia, J.-C. Lagier, and D. Raoult, “The aerobic activity of metronidazole against anaerobic bacteria,” *International Journal of Antimicrobial*

Agents, vol. 45, no. 5, pp. 537–540, 2015.

[22] A. Hernández Ceruelos, L. C. Romero-Quezada, J. C. Ruvalcaba Ledezma, and L. López Contreras, “Therapeutic uses of metronidazole and its side effects: an update,” *European Review for Medical and Pharmacological Sciences*, vol. 23, no. 1, pp. 397–401, 2019.

[23] J. Han, L. Zhang, S. Yang, J. Wang, and D. Tan, “Detrimental Effects of Metronidazole on Selected Innate Immunological Indicators in Common Carp (Cyprinus carpio L.),” *Bulletin of Environmental Contamination and Toxicology*, vol. 92, no. 2, pp. 196–201, 2014.

[24] A. Mishra, A. Kumar, A. Mishra, and H. Mishra, “Development of ultraviolet spectroscopic method for the estimation of metronidazole benzoate from pharmaceutical formulation,” *Journal of Natural Science, Biology and Medicine*, vol. 5, no. 2, p. 261, 2014.

[25] S. Tan, J. Jiang, B. Yan, G. Shen, and R. Yu, “Preparation of a novel fluorescence probe based on covalent immobilization by emulsion polymerization and its application to the determination of metronidazole,” *Analytica Chimica Acta*, vol. 560, no. 1–2, pp. 191–196, 2006.

[26] H. M. Maher, R. M. Youssef, R. H. Khalil, and S. M. El-Bahr, “Simultaneous multiresidue determination of metronidazole and spiramycin in fish muscle using high performance liquid chromatography with UV detection,” *Journal of Chromatography B*, vol. 876, no. 2, pp. 175–181, 2008.

[27] R. W. Murray, “Chemically modified electrodes,” *Accounts of Chemical Research*, vol. 13, no. 5, pp. 135–141, 1980.

[28] W. D. Adane, B. S. Chandravanshi, and M. Tessema, “A novel electrochemical sensor for the detection of metronidazole residues in food samples,” *Chemosphere*, vol. 359, p. 142279, 2024.

[29] S. Meenakshi, R. Rama, K. Pandian, and S. C. B. Gopinath, “Modified electrodes for electrochemical determination of metronidazole in drug formulations and biological samples: An overview,” *Microchemical Journal*, vol. 165, p. 106151, 2021.

[30] A. Joshi and K.-H. Kim, “Recent advances in nanomaterial-based electrochemical detection of antibiotics: Challenges and future perspectives,” *Biosensors and Bioelectronics*, vol. 153, p. 112046, 2020.

[31] K. Nejati and K. Asadpour-Zeynali, “Electrochemical synthesis of nickel–iron layered double hydroxide: Application as a novel modified electrode in electrocatalytic reduction of metronidazole,” *Materials Science and Engineering: C*, vol. 35, pp. 179–184, 2014.

[32] A. T. E. Vilian *et al.*, “Hierarchical dense Ni–Co layered double hydroxide supported carbon nanofibers for the electrochemical determination of metronidazole in biological samples,” *Electrochimica Acta*, vol. 354, p. 136723, 2020.

[33] M. Yang *et al.*, “Sensitive Voltammetric Detection of Metronidazole Based on Three-Dimensional Graphene-Like Carbon Architecture/Polythionine Modified Glassy Carbon Electrode,” *Journal of The Electrochemical Society*, vol. 165, no. 11, pp. B530–B535, 2018.

[34] P. Veerakumar, A. Sangili, S.-M. Chen, and K.-C. Lin, “Ultrafine gold nanoparticle embedded poly(diallyldimethylammonium chloride)–graphene oxide hydrogels for voltammetric determination of an antimicrobial drug (metronidazole),” *Journal of Materials Chemistry C*, vol. 8, no. 22, pp. 7575–7590, 2020.

[35] C. Li *et al.*, “Petal-like graphene–Ag composites with highly exposed active edge sites were designed and constructed for electrochemical determination of metronidazole,” *RSC Advances*, vol. 6, no. 51, pp. 45202–45209, 2016.

[36] J. Kalaiyarasi and K. Pandian, “Egg-Shell Like Hollow Alumina Sphere Modified Electrode for Enhanced Electrochemical Determination of Metronidazole,” *Journal of The Electrochemical Society*, vol. 166, no. 13, pp. B1151–B1160, 2019.

[37] S. Meenakshi, K. Pandian, L. S. Jayakumari, and S. Inbasekaran, “Enhanced amperometric detection of metronidazole in drug formulations and urine samples based on chitosan protected tetrasulfonated copper phthalocyanine thin-film modified glassy carbon electrode,” *Materials Science and Engineering: C*, vol. 59, pp. 136–144, Feb. 2016.

[38] S. Tursynbolat, Y. Bakytkarim, J. Huang, and L. Wang, “Ultrasensitive electrochemical determination of metronidazole based on polydopamine/carboxylic multi-walled carbon nanotubes nanocomposites modified GCE,” *Journal of Pharmaceutical Analysis*, vol. 8, no. 2, pp. 124–130, Apr. 2018.

[39] J. Huang, X. Shen, R. Wang, Q. Zeng, and L. Wang, “A highly sensitive metronidazole sensor based on a Pt nanospheres/polyfurfural film modified electrode,” *RSC Advances*, vol. 7, no. 1, pp. 535–542, 2017.