Proceeding of International Joint Conference on UNESA
Homepage : https://proceeding.unesa.ac.id/index.php/pijcu
e-ISSN : 3032-3762

PIJCU, Vol. 3, No. 1, December 2025
Page 1-10

Preliminary Study of Modified Iron Electrodes for Ammonia Nitrogen Detection Using Voltammetry Method

Erna Fitriany[1,3], Fredy Kurniawan[1*], Muji Harsini[2]
[1*] Department of Chemistry, Faculty of Science and Data Analytics, Institut Teknologi Sepuluh Nopember Surabaya (ITS), Surabaya, Indonesia, 60111.
[2]Department of Chemistry, Faculty of Science and Technology, Universitas Airlangga, Surabaya, Indonesia, 60115.
[3]Akademi Farmasi Mitra Sehat Mandiri Sidoarjo, Sidoarjo, Indonesia, 61262

Keywords:
Ammonia nitrogen
Electrochemistry
Iron
Cuprous oxide

ABSTRACT

A modified iron electrode was successfully fabricated for the electrochemical detection of ammonia nitrogen through its interaction with oxalate ions. The modification process involved immersing an iron wire in a 0.5 M $CuSO_4$ solution, followed by coating and subsequent treatment in a 50% H_2O_2 solution to accelerate surface oxidation. The electrochemical performance of the modified electrode was evaluated using cyclic voltammetry (CV) within a potential window of –0.4 to +0.6 V. For comparison, an unmodified iron electrode was also examined under identical conditions. The unmodified electrode exhibited no observable oxidation or reduction peaks, whereas the modified electrode demonstrated a distinct oxidation peak at +0.09 V, confirming its sensitivity toward oxalate ions. Further optimization was performed by varying the scan rate at 25, 50, 75, 100, 150, and 200 mV s^{-1}. The highest response was achieved at a scan rate of 100 mV s^{-1}, indicating optimal electrode kinetics. Calibration experiments with ammonia nitrogen concentrations ranging from 10 μM to 100 μM revealed a linear current response, described by the regression equation $y = 0.0033x + 0.0591$($R^2 = 0.9998$). These results clearly demonstrate the potential of the modified iron electrode as a reliable sensor for ammonia nitrogen detection.

INTRODUCTION

Ammonia nitrogen is widely recognized as one of the most critical parameters for evaluating water quality, primarily due to its potential transformation into nitrite, a compound associated with serious human health risks, including methemoglobinemia and other toxic effects (Cui et al., 2023). The accurate and timely determination of ammonia nitrogen in natural waters plays an essential role in environmental monitoring and public health protection. Traditional analytical techniques, such as spectrophotometric and titrimetric methods, are still widely employed; however, they often require lengthy sample preparation, rely on costly or toxic reagents, and demand laboratory-based operations, limiting their feasibility for rapid, on-site measurements (Duan et al., 2020; Ramadhan et al., 2025). To overcome these limitations, electrochemical detection has emerged as a powerful and practical alternative (Huo, n.d.; Sari et al., 2024). This approach offers several advantages, including lower operational costs, improved selectivity, high sensitivity, and simplified procedures, making it particularly suitable for field applications (G. Wang et al., 2022). Additionally, ammonia gas-sensitive electrodes (Tian et al., 2022), and ammonium ion-selective electrodes (Krivačić et al., 2024; Q. Wang et al., 2024). have shown great promise for achieving accurate, real-time measurements in complex aqueous environments. Collectively, these innovations highlight the potential of electrochemical sensing systems as efficient tools for continuous monitoring of ammonia nitrogen in diverse water systems.

Compared with other metals such as Pt and Au, iron is more cost-effective. Meanwhile, the metal oxides CuO and Cu_2O can be used as co-catalysts to increase the detection sensitivity of the working electrode. Cu_2O is a p-type semiconductor material with a cubic crystal structure and unique electronic properties, with holes as the dominant charge carriers. These characteristics have led to its widespread development for electrochemical applications, particularly in sensors based on electrode modifications. (band gap of 2.17 eV) (Liu et al., 2021), non-toxic, easy to produce and store, and high specific capitance. Several recent studies have demonstrated the versatility of Cu_2O-based nanomaterials in the development of highly sensitive electrochemical sensors. For instance, Ag–Cu_2O/Ti_3C_2 composites have been successfully applied in the fabrication of a galactose detection biosensor (Fu et al., 2022). Similarly, $Cu_2O@Cu_9S_5$ egg yolk shell nanospheres have been employed as an efficient sensing platform for hydrogen peroxide (H_2O_2) detection (Li et al., 2022). In another approach, Cu_2O nanocrystals integrated with a gold electrode have shown excellent performance in the electrochemical detection of p-chloronitrobenzene in aqueous media (Chakraborty et al., 2022). Furthermore, Cu_2O–CuO nanoparticles supported on carbon nanotubes have been utilized for the rapid and reliable quantification of glucose, highlighting their practical potential in biomedical and environmental applications (Z. Wang et al., 2022). These examples collectively illustrate the broad applicability of Cu_2O-based hybrid systems in designing advanced electrochemical sensors.

The developed Cu_2O–modified iron electrode demonstrates high sensitivity toward ammonia nitrogen due to the synergistic interaction between Cu_2O and the iron substrate. The semiconducting nature of Cu_2O enhances charge carrier mobility and facilitates rapid electron transfer during the electrochemical oxidation or reduction of ammonia species at low concentration. Meanwhile, the iron substrate provides a conductive backbone and additional catalytic sites that promote the adsorption and subsequent electron exchange of ammonia nitrogen molecules. The porous and heterogeneous surface morphology formed during the immersion–oxidation modification increases the effective electroactive surface area, enabling more analyte molecules to interact simultaneously with the electrode surface. Furthermore, Cu_2O contributes to improved mass transport and faster diffusion of ammonia nitrogen toward active sites, leading to higher current responses even at low analyte concentrations. This combination of enhanced electron transfer kinetics, high surface reactivity, and stable semiconductor behavior makes the Cu_2O–modified iron electrode a highly sensitive and reliable sensing platform for ammonia nitrogen detection under neutral conditions. Consequently, this sensor can accurately detect trace levels of ammonia nitrogen, offering both rapid response and long-term operational stability.

RESEARCH METHOD

2.1 Reagents and apparatus

Copper(II) sulphate pentahydrate ($CuSO_4.5H_2O$), ammonium Chloride (NH_4Cl), sodium dihydrogen phospate monohydrate ($NaH_2PO_4.H_2O$), disodium hydrogen phospate anhydrous (Na_2HPO_4), and trisodium phospate (Na_3PO_4) were purchased from Sigma-Aldrich (USA). Ultra High Pure Water was supplied by PT. Brataco, Indonesia. Iron (Fe)

were sourced from local market. The electrochemical measurements were using an Autolab PGSTAT128 N potensiostat/galvanostat, controlled by Nova software version 2.1.6. surface morphology characterization was using a Hitachi SU 8220 FESEM-EDX at Chemistry Laboratory, ITS. The crystalline structure of the electrode was analyzed using Philips XRD at the Energy and Materials laboratory, ITS.

2.2 Preparation of modified iron electrodes

Iron wire (5 cm) was used as a substrate. The surface of the iron wire is rubbed evenly to clean all rust and oxide, as well as contaminants on the surface of the iron wire. The iron wire was then soaked in a 0.5 M $CuSO_4.5H_2O$ solution for 5 minutes. During immersion, Cu^{2+} ions were spontaneously reduced to metallic Cu^0 on the iron surface owing to the difference in standard reduction potentials between Fe (-0.44 V) (eq. 1) and Cu (+0.34 V) (eq.2).

$Fe(s) \rightarrow Fe^{2+} + 2e^-$, E^o= -0.44 V (anode) (1)

$Cu^{2+} + 2e^- \rightarrow Cu(s)$, E^o= +0.34 V (cathode) (2)

Immediately after removal, the Cu-coated substrate was oxidized in H_2O_2 solution for 1 minutes, resulting in the formation of a dark-red Cu_2O layer on the surface of Fe.

2.3 Electrochemical measurement

Electrochemical measurements were performed by AUTOLAB PGSTAT-13 electrochemical workstation (Eco-Chemie, The Netherlands). A standard three-electrode electrochemical cell was used. The working electrode (Fe/Cu_2O) is iron modified electrode, Ag/AgCl (sat) as the reference electrode, and a Pt wire as counter electrode. The potential in all figures are indicated relative this reference electrode. The measurements were performed at various concentrations of NH_4Cl in 0.1 PBS pH= 7.0. Scan rate optimization in this study was carried out by varying the scan rate starting from 25 mV/s; 50 mV/s; 75 mV/s; 100 mV/s; and 100 mV/s. This stage is used to determine the best scan rate which will then be used in subsequent measurements. Determination of detection limits and sensitivity, as well as electrochemical reactions on the electrode surface, was carried out by varying the concentration of NH_4Cl, 10- 100 μM.

RESULTS AND DISCUSSION

3.1 Electrocatalytic performance of different modified iron electrodes

The electrocatalytic activity of three different electrodes based on iron electrodes in Phospate Buffer Solution (PBS) was shown in Fig. 1. In the CV curve characteristic of Fe, Cu, and modified iron electrodes (Fe/Cu_2O). There was a different characteristics, Fe electrodes and Cu electrodes is not sensitive to NH_4Cl solutions. In contrast, the modified iron electrodes exhibit sensitivity to NH_4Cl. The modified electrode exhibits superior electron transfer capabilities compared to Fe and Cu electrodes without modification, as evidenced by its higher current response These results indicate that electron transfer occurs with a higher level of efficiency, influenced by the strong synergy between the Fe and Cu_2O materials on the electrode surface. This interaction results in increased electrocatalytic activity and sensor system stability. This electrode selected for next experimental investigations. In general, oxidation reactions offer potential for

quantitative analysis and contingent upon parameters such as reaction mechanisms. After adding ammonium chloride, the modified electrode showed an oxidation peaks at +0.09V, revealing the oxidation process of NH_4Cl on the surface of the electrode. Based on the new mechanism of two electron for ammonium ions (NH_4^+) migrates to the surface electrodes, then it will be dissociated an adsorbed on the surface of the electrode. The generated H is involved in two electron and produce *OOH and *HOOH. Cu_2O will enhanced the adsorption of O_2 and which make this modified electrode is suitable for NH_4^+ detection in neutral conditions (Z. Wang et al., 2022).

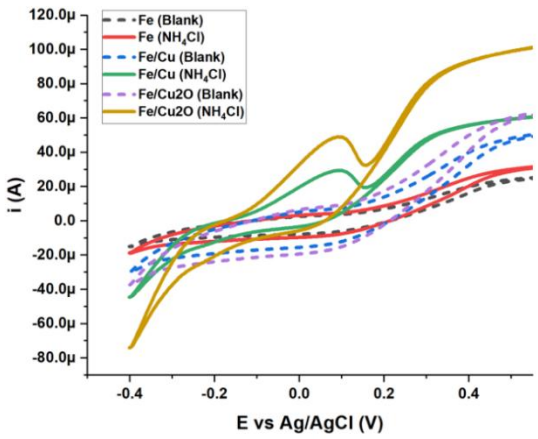

Fig. 1. CV measurements of the Fe, Cu, Fe/Cu_2O electrode in 0.1 M PBS solution, with and without NH_4Cl at a scan rate 100 mV/s.

3.2 Kinetic analysis of the determination of NH_4Cl

The influence of scan rate on the electrochemical behavior of modified iron electrodes toward the oxidation of ammonium chloride (NH_4Cl) was systematically evaluated using CV. As shown in **Fig. 2**, the anodic peak current (I_{pa}) exhibited a gradual increase with increasing scan rate, demonstrating a strong linear relationship between the peak current and the sweep rate. The regression equation, expressed as I_{pa} (μA) = 4.942v + 53.5 with a correlation coefficient (R^2 = 0.9946), confirms the excellent proportionality between current response and scan rate. This relationship indicates that the electrochemical oxidation of NH_4Cl at the modified iron electrode is predominantly governed by a diffusion-controlled mechanism.

Table 1. Correlation between scan rates (mV/s) vs Ipa (μA)

No.	Scan rates (mV/s)	Ipa (μA)
1	10	20.2
2	25	24.8
3	50	30.3
4	75	34.9
5	100	49.7
6	150	54.2
7	175	58.7
8	200	64.3

Among the tested conditions, a scan rate of 100 mV/s was identified as the optimal value, providing a well-defined redox peak with high signal stability and reproducibility. At this scan rate, the balance between current sensitivity and signal resolution was achieved, minimizing kinetic limitations while ensuring reliable detection (Mulyawati et al., 2025). These findings underscore the crucial role of scan rate optimization in enhancing electrode performance for diffusion-driven redox systems.

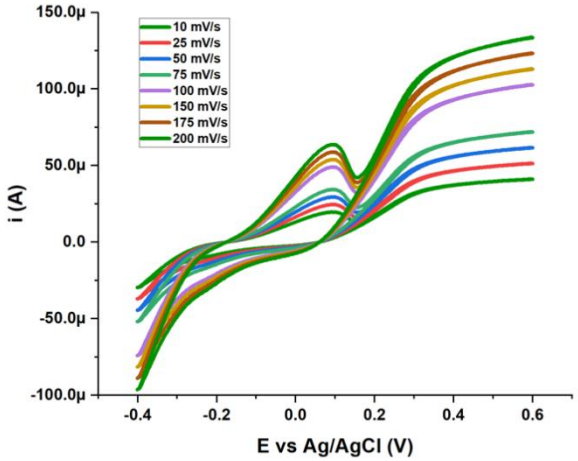

Fig.2. CV responses of 20 µM ammonia chloride at the iron modified electrode in 0.1 M PBS pH 7 at different scan rates from 10 mV/s – 200 mV/s.

3.3 pH Analysis

The effect of pH is a decisive parameter in electrochemical analysis, as it governs electrode performance, analyte stability, and the underlying electron-transfer mechanism. To examine this influence, CV experiments were conducted using 20 µM ammonium chloride solutions at pH values ranging from 3 to 10. The recorded voltammograms exhibited anodic peaks corresponding to the oxidation of ammonium ions (NH_4^+), as presented in **Fig. 3.** At acidic pH values below the pKa of NH_4^+, higher anodic currents were observed, reflecting enhanced oxidation activity. This increase can be explained by the abundance of protons that facilitate proton-coupled electron transfer, thereby lowering the activation barrier of the oxidation process. At pH values below the pKa of NH_4^+ (approximately 9.25), the solution environment is dominated by the protonated form of ammonia, i.e., NH_4^+, rather than the neutral NH_3 species. Under these acidic conditions, the high proton concentration enhances proton-coupled electron transfer (PCET) processes at the electrode surface. This is because the excess H^+ ions can participate directly in the oxidation mechanism or stabilize intermediate species, leading to lower activation energy for electron transfer. Additionally, maintaining the pH below the pKa ensures the predominance of NH_4^+, which is the actual electroactive species involved in the observed anodic process. Consequently, the increased anodic current at acidic pH reflects both the higher availability of NH_4^+ and the facilitative role of protons

in the oxidation reaction.However, excessive proton availability may also promote competing reactions, which could reduce the selectivity and reproducibility of the sensor response. The electrochemical oxidation of NH_4^+ is typically associated with multistep pathways, where NH_4^+ can be oxidized to nitrogen gas (N_2), nitrite (NO_2^-), or nitrate (NO_3^-), depending on the electrode material and reaction environment. A representative half-reaction can be expressed as:
$NH_4^+ + 3H_2O \rightarrow NO_2 + 8H^+ + 6\ e^-$ (Lu et al., 2023)

At neutral pH (pH 7), the process favors the direct oxidation of NH_4^+ without excessive proton interference, ensuring stable electron transfer and improved analytical reproducibility. For this reason, pH 7 was selected as the optimal working condition for subsequent oxalate detection, allowing the oxidation to proceed via the stable NH_4^+ pathway with minimal side reactions.

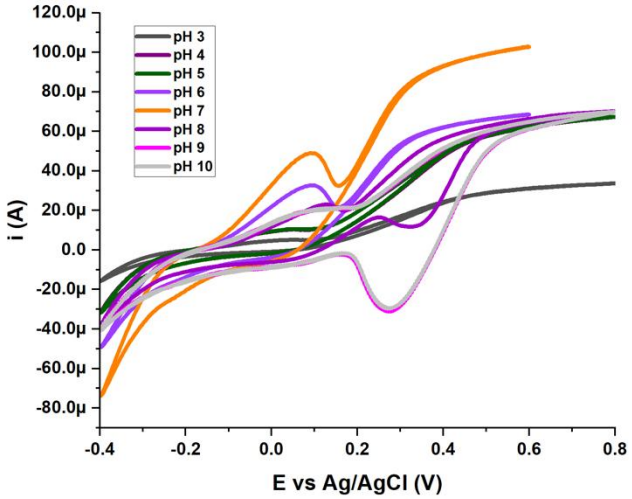

Fig.3. CV curves of 20 mM ammonium chloride at the modified iron electrodes in different pH values.

3.4 Electrocatalytic oxidation of ammonium

The electrochemical oxidation behavior of ammonium ions (NH_4^+) at the surface of the modified electrode was systematically investigated using CV. Fig. 4 presents the voltammetric response obtained under varying concentrations of ammonium chloride, ranging from 10 to 100 µM. The results demonstrate that the anodic peak current (Ipa) increases proportionally with the rise in NH_4Cl concentration, confirming a concentration-dependent oxidation process. The linear regression equation, Ipa = 0.0033 [NH_4^+] + 0.0591 with an excellent correlation coefficient (R^2 = 0.9998), highlights the strong quantitative relationship between analyte concentration and current response. During the oxidation of ammonia or ammonium ions, electrons are transferred from nitrogen-containing species to the electrode, forming intermediate products such as nitrogen gas (N_2), nitrite (NO_2^-), or nitrate (NO_3^-), depending on the electrode material and potential range. These oxidation products are stable and do not readily undergo a reverse reduction reaction during the reverse scan. As a result, when the potential is swept back, there are no electroactive species available to be reduced, leading to the

absence of a corresponding cathodic peak. Additionally, the oxidation of ammonia involves multi-step chemical and electrochemical reactions, often accompanied by proton release and adsorption processes. These steps tend to shift the reaction equilibrium toward oxidation and further suppress the reversibility of the system. The strong adsorption of intermediates or the evolution of gaseous products (such as N_2) can also hinder the regeneration of the original species, which prevents the cathodic peak from appearing.

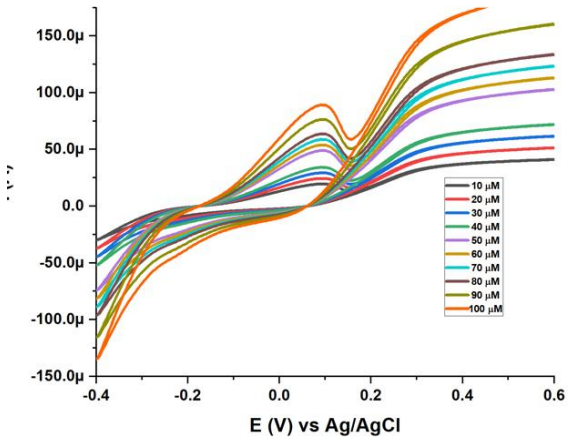

Fig.4. CV curves of 10-100 µM ammonium chloride in PBS 0.1M pH 7.

This proportional increase in Ipa can be attributed to the enhanced availability of NH_4^+ species at the electrode surface, which facilitates electron transfer during the oxidation reaction. As the concentration of ammonium ions increases, more electroactive sites participate in the redox process, thereby generating higher current responses. The observed behavior is consistent with diffusion-controlled oxidation mechanisms, where the flux of NH_4^+ to the electrode surface governs the reaction kinetics. These findings not only validate the sensitivity of the modified electrode but also underline its potential application for quantitative determination of ammonium in aqueous systems, with high accuracy and reproducibility over a wide concentration range.

CONCLUSION

A simple yet effective modified iron electrode was successfully fabricated and demonstrated superior electrocatalytic activity toward the oxidation of ammonium ions (NH_4^+). Compared with unmodified Fe and Cu electrodes, the Fe/Cu_2O electrode exhibited enhanced electron transfer capability, highlighting the synergistic contribution of Cu_2O to the surface properties. Cyclic voltammetry results confirmed that the electrochemical process is diffusion-controlled, with a scan rate of 100 mV/s identified as the optimal condition to achieve a balance between sensitivity, resolution, and stability. Furthermore, pH studies revealed that neutral pH (7.0) provides the most favorable environment for direct NH_4^+ oxidation, ensuring reproducible signals without interference from proton-driven side reactions. Concentration-dependent analysis

showed a strong linear correlation between anodic peak current and NH_4^+ concentration, with excellent regression values. Overall, the modified iron electrode offers a simple, low-cost, and reliable sensing platform with promising potential for quantitative ammonium detection in aqueous systems.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support provided by Beasiswa Pendidikan Indonesia (BPI) through the Lembaga Pengelola Dana Pendidikan (LPDP), Ministry of Finance of the Republic of Indonesia. This support was instrumental in facilitating the completion of this research. The authors also express sincere appreciation to all institutions and individuals who contributed to the successful implementation of this study.

REFERENCES

Chakraborty, U., Kaur, I., Bhanjana, G., Kumar, S., Kaur, G., Kaushik, A., & Chaudhary, G. R. (2022). Cuprous oxide nanocubes for simultaneous electrochemical detection and photocatalytic degradation of para-chloronitrobenzene. Journal of Environmental Chemical Engineering, 10(6), 108662. https://doi.org/10.1016/j.jece.2022.108662

Cui, J., Hou, J., Pan, H., & Kang, P. (2023). Self-supporting CuM LDH (M = Ni, Fe, Co) carbon cloth electrodes for selective electrochemical ammonia oxidation to nitrogen. Journal of Electroanalytical Chemistry, 940, 117502. https://doi.org/10.1016/j.jelechem.2023.117502

Duan, G. Y., Ren, Y., Tang, Y., Sun, Y. Z., Chen, Y. M., Wan, P. Y., & Yang, X. J. (2020). Improving the Reliability and Accuracy of Ammonia Quantification in Electro- and Photochemical Synthesis. ChemSusChem, 13(1), 88–96. https://doi.org/10.1002/cssc.201901623

Fu, M., Liu, M., Wu, X., Cai, Z., Zhang, X., Xi, Z., Wang, Y., Dai, C., Kang, X., Liu, Z., Miao, B., & Gao, F. (2022). A novel ternary Ag-Cu2O/Ti3C2 heterostructure with high peroxidase-like activity for on-site colorimetric detection of galactose. Sensors and Actuators B: Chemical, 369, 132343. https://doi.org/10.1016/j.snb.2022.132343

Huo, X. (n.d.). Cu2ZnSnS4/CeO2 heterojunction with excellent sensing property for ammonia nitrogen in aqueous solution—IOPscience. Retrieved September 11, 2025, from https://iopscience.iop.org/article/10.1088/1361-6641/ac0b94

Krivačić, S., Boček, Ž., Zubak, M., Kojić, V., & Kassal, P. (2024). Flexible ammonium ion-selective electrode based on inkjet-printed graphene solid contact. Talanta, 279, 126614. https://doi.org/10.1016/j.talanta.2024.126614

Li, W., Liu, J., Chen, C., Zhu, Y., Liu, N., Zhou, Y., & Chen, S. (2022). High catalytic performance non-enzymatic H2O2 sensor based on Cu2O@Cu9S5 yolk-shell nanospheres. Applied Surface Science, 587, 152766. https://doi.org/10.1016/j.apsusc.2022.152766

Liu, S., Jiang, X., Waterhouse, G. I. N., Zhang, Z.-M., & Yu, L. (2021). A Cu2O/PEDOT/graphene-modified electrode for the enzyme-free detection and quantification of glucose. Journal of Electroanalytical Chemistry, 897, 115558. https://doi.org/10.1016/j.jelechem.2021.115558

Lu, H., Hu, J., Zhang, S., Long, M., & Tang, A. (2023). Cuprous oxide and Ag modified titanium dioxide electrode for ultra-sensitive detection of ammonia nitrogen. Journal of Electroanalytical Chemistry, 949, 117842. https://doi.org/10.1016/j.jelechem.2023.117842

Mulyawati, M., Madurani, K. A., Ulfin, I., Sari, N. P., & Kurniawan, F. (2025). Development of a copper-modified iron electrode electrochemical sensor for sensitive detection of oxalic acid. Materials Chemistry and Physics, 344, 131063. https://doi.org/10.1016/j.matchemphys.2025.131063

Ramadhan, M. R., Destiny, K. D., Leoriza, M. D., Sabriena, N., Kurniawan, F., Ismail, A. I., Handayani, M., Ogata, G., Einaga, Y., & Triana, Y. (2025). Electrochemical behaviour of amodiaquine detection using boron doped diamond electrodes. International Journal of Electrochemical Science, 20(1), 100913. https://doi.org/10.1016/j.ijoes.2024.100913

Sari, N. P., Mulyawati, M., Syahputra, M. Y., Madurani, K. A., & Kurniawan, F. (2024). A Novel ultrasensitive nitrite ion detection using tungsten trioxide-modified gold electrode. Electrochimica Acta, 497, 144590. https://doi.org/10.1016/j.electacta.2024.144590

Tian, X., Yao, L., Cui, X., Zhao, R., Chen, T., Xiao, X., & Wang, Y. (2022). A two-dimensional Ti3C2TX MXene@TiO2/MoS2 heterostructure with excellent selectivity for the room temperature detection of ammonia. Journal of Materials Chemistry A, 10(10), 5505–5519. https://doi.org/10.1039/D1TA10773A

Wang, G., Gao, J., Sun, B., He, D., Zhao, C., & Suo, H. (2022). Enhanced ammonia sensitivity electrochemical sensors based on PtCu alloy nanoparticles in-situ synthesized on carbon cloth electrode. Journal of Electroanalytical Chemistry, 922, 116721. https://doi.org/10.1016/j.jelechem.2022.116721

Wang, Q., Wu, Q., Zhao, M., Lu, S., & Liang, D. (2024). Prussian blue analogue based integrated membrane electrodes for desalination and selective removal of ammonium ions in a rocking-chair capacitive deionization. Chemical Engineering Journal, 482, 148923. https://doi.org/10.1016/j.cej.2024.148923

Wang, Z., Liu, Y., Cheng, Y., Men, Y.-L., Liu, P., Zhang, L., Dai, B., & Pan, Y.-X. (2022). Fast and efficient electrocatalytic oxidation of glucose triggered by Cu2O-CuO nanoparticles supported on carbon nanotubes. Frontiers in Chemistry, 10. https://doi.org/10.3389/fchem.2022.998812