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Electrochemical Detection of Fe²⁺ ions in Water using 2-Dimensional g-C₃N₄ modified Glassy Carbon Electrode-based Sensor

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Abstract—This work presents a 2-Dimensional (2D) Graphitic carbon nitride (g-C₃N₄) modified glassy carbon electrode (GCE)-based electrochemical sensor for detection of Fe²⁺ ions in water. The 2D g-C₃N₄ nanomaterial is prepared by dispersing, ultra-sonification and then modifying the GCE using the drop-casting method. The structural and morphological characteristics of the prepared g-C₃N₄ are examined using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The performance of the sensor is analysed for different concentrations (from 0.9 mM to 5 mM) of iron content in the electrolyte using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The obtained results indicate excellent sensing performance towards target ions. Along with the concentration study, the accumulation study (with a scan speed of 10 mV/s to 1000 mV/s in -0.6 V to 0.8 V region) and repeatability analysis (30 CV scans) are also carried out. Based on the obtained results, the 2D g-C₃N₄ modified sensor work is a promising candidate for electrochemical detection of Fe²⁺ ions in water for a wide range of applications.

Keywords— *Electrochemical sensor; g-C₃N₄; glassy carbon electrode; Fe²⁺ ions detection.*

I. INTRODUCTION

Iron plays a major role in both biological and environmental systems. It exists in water, as many other minerals that are present in the earth's crust. The human body requires an average of 8 to 12 mg of iron every day for vital functioning of organs. For example, iron is required for blood to carry oxygen in the body. The deficiency may cause fatigue, anaemia, etc. The presence of iron traces in water resources is also crucial for aquatic life. However, the higher concentration of iron in water resources could also severely damage the biological organs as heavy metal ions are hazardous and non-biodegradable [1]. For this reason, routine monitoring of iron quality in water resources such as lakes, river, and ponds is critical [2].

The typical methods for evaluation of water quality include spectrophotometric, and calorimetric analysis. Often these methods require lab-based analysis and difficult to conduct in field. Considering the varying quality of water at a place (e.g., due to environmental factors such as rain, or human factors such as release of waste chemical in water bodies) it is desirable to have compact and cheaper sensors for onsite monitoring [3, 4]. Further, the electrochemical sensors are expected to have fast response, high sensitivity, and good

selectivity [5, 6]. Herein, we present a 2-Dimensional (2D) Graphitic carbon nitride (g-C₃N₄) modified glassy carbon electrode (GCE) based electrochemical sensor for detection of Fe²⁺ ions in water. The 2D g-C₃N₄ nanosheet used in this work as the sensing layer is an eco-friendly material. The presented sensor shows excellent response in the tested range of water having 0.9 mM to 5 mM of iron.

This paper is organised as follows: Section II presents various materials and methods used in this work to develop the sensors. This is followed by presentation of results in Section III and summary of key outcomes in Section IV.

II. MATERIAL AND METHODS

A. Material

Melamine, Phosphate buffer solution tablets (PBS), Dimethylformamide (DMF), and Iron(II) chloride salt were purchased from Merck. Carbon paste was purchased from Sun Chemical. All materials are used without any further modification.

B. Synthesis of g-C₃N₄ and Modification

Thermal condensation and evaporation of melamine were carried out to synthesize a pristine g-C₃N₄ powder. The 2D g-C₃N₄ nanomaterial was prepared by dispersing 20 mg of g-C₃N₄ in 1 ml of DMF solvent using probe ultra-sonification. To modify the GCE, 5 μ l of the dispersed g-C₃N₄ solution was drop casted four times – each time with a drying period of 15 mins in an oven at 60 °C. [7]

C. Electrochemical Measurements

The electrochemical behaviour of g-C₃N₄ modified GCE for the detection of targeted analyte i.e., Fe²⁺ ions was studied using Cyclic Voltammetry and Differential Pulsed Voltammetry methods. *Metrohm Autolab (PGSTAT302N)* electrochemical workstation was used for these studies. Here, 0.1 M of PBS solution was maintained as the initial blank electrolyte solution with a pH of 7, in order to provide an ionic medium for charge transfer and to resemble a neutral water environment. The 0.1 M of PBS solution was prepared by adding 1 tablet of commercial PBS into deionized water (DI). CV measurements were made over the potential range of -0.6 V to 0.8 V. Similarly, DPV measurements were made with the modulation amplitude of 0.05 V, modulation time of 0.25 s, and step potential of 5 mV. To vary the concentration of analyte solution, Fe²⁺ stock solutions of 100 mM and 0.1 mM were prepared by mixing FeCl₂ salt in DI water, and further,

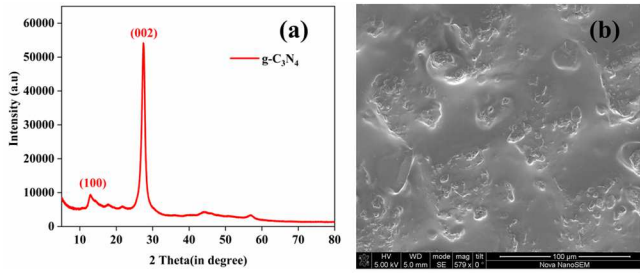


Fig. 1. (a) XRD pattern for $g\text{-C}_3\text{N}_4$ powder. (b) SEM images of $g\text{-C}_3\text{N}_4$ coated carbon layer.

they were added with the 0.1 M PBS solution to make 0.9 mM to 5 mM solution.

III. RESULTS AND DISCUSSION

A. Material Characterisation

The prepared $g\text{-C}_3\text{N}_4$ salts were characterized by X-Ray diffraction patterns. Fig. 1(a) shows that the peak obtained from the XRD for the prepared salt. The peaks at 12.96 and 27.46 indicate the lattice planes of (100) and (002) of $g\text{-C}_3\text{N}_4$ respectively. This is also confirmed using the ICDD card 00-066-0813. The SEM image for the coated $g\text{-C}_3\text{N}_4$ layers over the screen-printed carbon paste substrate (similar to the glassy carbon surface) is shown in Fig. 1(b). This indicates multiple coated layers having a homogenous surface over the substrate without any cracks or nanopores. These results also signify the well spread of 2D nanomaterial with uniformity.

B. Electrochemical detection of Iron ions (Fe^{2+})

Fig. 2(a) represents the system diagram of the 3-electrode system used for the detection of iron. Here, the platinum coil was used as a counter electrode (CE), the standard Ag/AgCl was used as a reference electrode (RE) and the $g\text{-C}_3\text{N}_4$ coated GC was used as a working electrode (WE). Fig. 2(b) shows the obtained CVs over the potential range of -0.6 V to 0.8 V in the absence and presence of 2.5 mM of Fe^{2+} ions in the electrolyte

solution. Here, the varied CV patterns indicate the occurrence of an electrochemical redox reaction. DPV patterns over the range of -0.2 V to 0.4 V, shown in Fig. 2(c), were obtained in the absence and presence of Fe^{2+} ions in 0.1 M of PBS solution. The peak displayed in the anodic current at -0.09 V is in response to the oxidation of Fe ions, that causes the addition of evolved $2e^-$ free electrodes. This leads to the increase in the current level, which can be seen through the emergence of DPV peak for the analyte solution in comparison with the blank solution. The electrochemical redox mechanism can be explained easily using the following chemical reactions i.e., Fe to $\text{Fe}^{2+} + 2e^-$ and vice versa.

C. Concentration study

For the concentration studies, both CV and DPV patterns were obtained at different concentrations (from 0.9 mM to 5 mM) of iron content in the electrolyte. In Fig. 2(d), the increase in the concentration of analyte leads to an increase in oxidation peak in the forward scan with a slight shift from 0.05 V to -0.1 V. In the reverse scan, the increase in reduction peak is in the region over -0.29 V to -0.38 V. Fig. 2(d) displays the DPV peak rising in anodic current over -0.06 V to -0.014 V in respect to the increased iron concentration in the electrolyte solution. To find the linearity for the peak rise, the peak current value for each concentration in the DPV pattern was plotted against their respective concentration, as shown in Fig. 2(f). It may be noted that there are two linear lines with the R^2 value of 0.9367 and 0.97233 over the concentration range of 1.0 to 1.5 mM and 2 to 5 mM respectively.

The linear equations for the above ranges were

$$I_p (\mu\text{A}) = 0.0612 \text{ Conc Fe}^{2+} (\text{mM}) - 0.8573$$

$$I_p (\mu\text{A}) = 0.70 \text{ Conc Fe}^{2+} (\text{mM}) - 0.5056$$

In the lower concentration region of 1.0 mM to 1.5 mM, the hexagonal core-shell structure of $g\text{-C}_3\text{N}_4$ may have caused the absorption of oxidized Fe^{2+} ions over the sensing layer, which leads to the blockage of most incoming free electrons

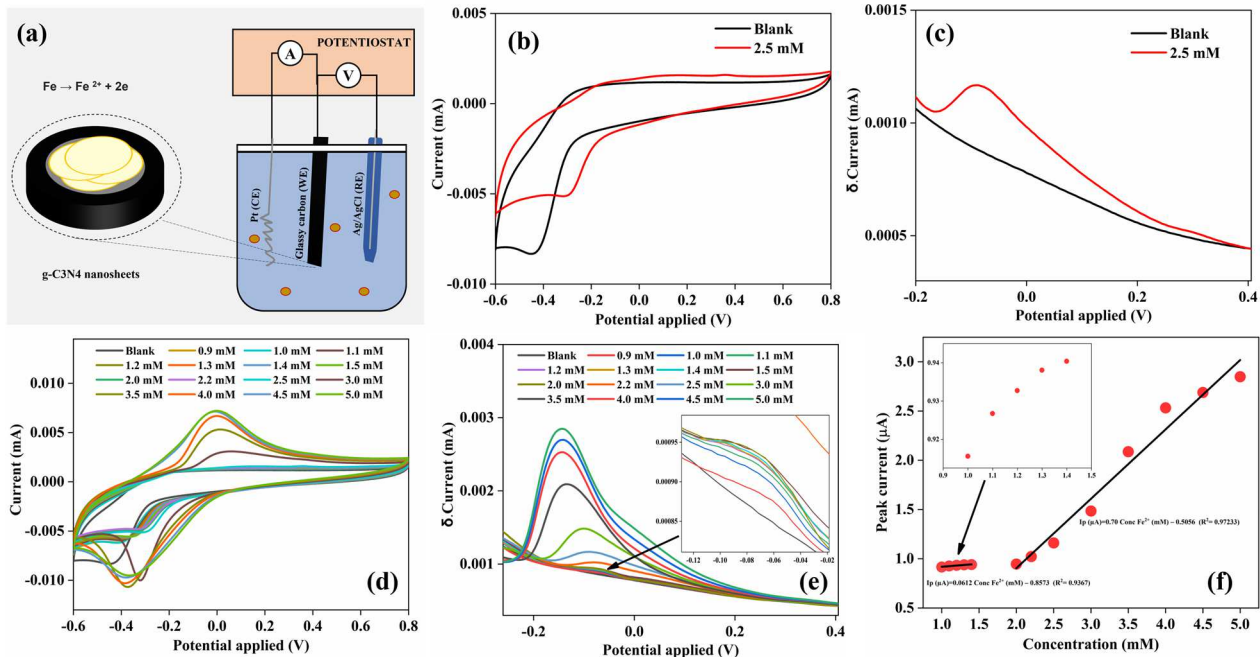


Fig. 2. (a) Experimental setup. (b, c) CV and DPV curve responses of $g\text{-C}_3\text{N}_4$ coated GCE in absence and presence of 2.5 mM of iron (Fe^{2+}) ions in PBS solution. (d, e) CV and DPV curve responses for detecting 0.9 mM to 5 mM iron ions in 0.1 M PBS. (f) Concentration of iron analyte vs oxidation peak current (I_p).

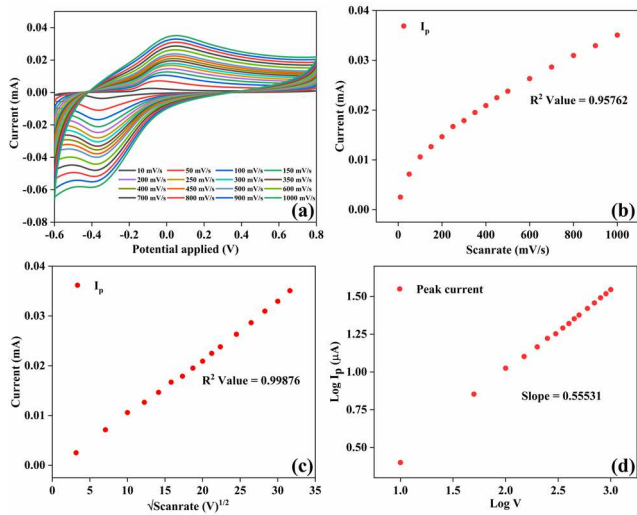


Fig. 3. (a) CV response curves for g-C₃N₄/GCE in 2.5 mM of Fe²⁺ ions in PBS with different scan rate of 10 to 1000 mV/s; (b) I_p versus scan rate; (c) I_p versus $\sqrt{\text{scan rate}}$; (d) log of I_p versus Log of scan rate.

for diffusion. For the higher concentration region, even though the deposited Fe²⁺ ions block the current path for incoming ions, the oxidation of the higher concentration of Fe²⁺ ions over the g-C₃N₄ nanosheet leads to excessive free electron charges, leading to a sudden rise in the peak observed after the formation the current path for the driving free electrons [8].

D. Accumulation study

For the accumulation study, The CV patterns were obtained for different scan rates to study their detection mechanisms. Fig. 3(a) displays the CV patterns over the region of -0.6 V to 0.8 V with the scan speed of 1 mV/s to 1000 mV/s for the detection of 1.5 mM Fe²⁺ ions in 0.1 M PBS electrolyte. The oxidation peak current value from the different scan rates was plotted against each other in Fig. 3(b). The R² value for the plotted peaks is 0.95762, which shows a highly linear relationship between the scan speed and peak current. This confirms the occurrence of an absorption-controlled mechanism. Fig. 3(c) displays higher linearity between the square root of scan speed and peak current with an R² value of 0.99876. This confirms the diffusion-controlled mechanism as well. From the scan speed studies, the mechanism occurring over the g-C₃N₄ layers were both absorption-controlled and diffusion-controlled. However, at higher concentrations of iron analyte detection, a diffusion-controlled mechanism plays a major role, which was confirmed by plotting Log V against Log I_p. Here the slope was found to be 0.55 which was closer to the ideal diffusion-controlled mechanism (0.5) [9].

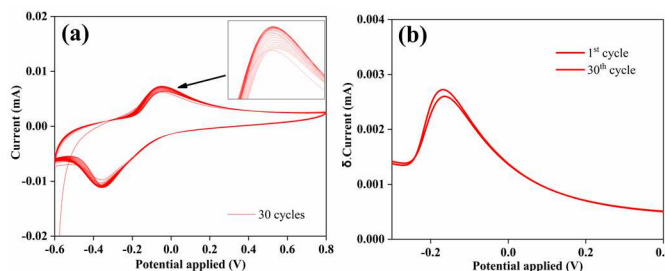


Fig. 4. (a) CV response of 30 scans in 2.5 mM of Fe²⁺ ions in PBS 50mV/s; (b) DPV response for the 1st and 30th consecutive cycles.

E. Repeatability

For the repeatability studies, a continuous cycle of 30 CV scans was obtained and the respective DPV patterns were obtained before and after scanning, as shown in Fig. 4 (a, b). From the repeatability study, it may be noted that a slight change in oxidation peak occurs for the initial scans and later these peaks converge to have a more reliable and accurate response.

IV. CONCLUSION

In summary, the 2D g-C₃N₄ nanomaterials-based sensor shows excellent response for the detection of iron in water. The performance of the sensor is examined for iron content concentrations ranging from 0.9 mM to 5 mM using CV and DPV techniques. Along with the concentration study, the accumulation study (with a scan speed of 10 mV/s to 1000 mV/s in -0.6 V to 0.8 V region) and repeatability analysis (30 CV scans) are also carried out. The electrodes on rigid substrates can be replaced with flexible, eco-friendly, biodegradable materials for easy disposability and practical field applications. This will be the focus of our future work.

REFERENCES

- [1] M. S. Rahman, and G. A. Gagnon, "Bench-scale evaluation of drinking water treatment parameters on iron particles and water quality," *Water Research*, vol. 48, pp. 137-147, 2014/01/01, 2014.
- [2] L. Manjakkal, S. Mitra, Y. R. Petillot, J. Shutler, E. M. Scott, M. Willander, and R. Dahiya, "Connected Sensors, Innovative Sensor Deployment, and Intelligent Data Analysis for Online Water Quality Monitoring," *IEEE Internet of Things Journal*, vol. 8, no. 18, pp. 13805-13824, 2021.
- [3] A. K. Aliyana, P. Ganguly, A. Beniwal, N. Kumar S K, and R. Dahiya, "Disposable pH sensor on paper using screen-printed graphene-carbon ink modified zinc oxide nanoparticles," *IEEE Sensors Journal*, 2022, DOI: 10.1109/JSEN.2022.3206212
- [4] S. Dervin, P. Ganguly, and R. S. Dahiya, "Disposable Electrochemical Sensor Using Graphene Oxide-Chitosan Modified Carbon-Based Electrodes for the Detection of Tyrosine," *IEEE Sensors Journal*, vol. 21, no. 23, pp. 26226-26233, 2021.
- [5] A. Beniwal, P. Ganguly, A. K. Aliyana, G. Khandelwal, and R. Dahiya, "Screen-printed Graphene-carbon Ink based Disposable Humidity Sensor with Wireless Communication," *Sensors and Actuators B: Chemical*, 2022. (in press)
- [6] G. Khandelwal, and R. Dahiya, "Self-Powered Active Sensing Based on Triboelectric Generators," *Advanced Materials*, vol. 34, no. 33, pp. 2200724, 2022.
- [7] Y. Zhang, Q. Pan, G. Chai, M. Liang, G. Dong, Q. Zhang, and J. Qiu, "Synthesis and luminescence mechanism of multicolor-emitting g-C₃N₄ nanopowders by low temperature thermal condensation of melamine," *Scientific Reports*, vol. 3, no. 1, pp. 1943, 2013/06/05, 2013.
- [8] M. Nguyen Van, O. L. T. Mai, C. Pham Do, H. Lam Thi, C. Pham Manh, H. Nguyen Manh, D. Pham Thi, and B. Do Danh, "Fe-Doped g-C₃N₄: High-Performance Photocatalysts in Rhodamine B Decomposition," *Polymers*, vol. 12, no. 9, pp. 1963, 2020.
- [9] D. K. Neethipathi, P. Ganguly, A. Beniwal, M. Scott, A. Bass, and R. Dahiya, "MoS₂ modified screen printed carbon electrode based flexible sensor for detection of Copper," *IEEE Int. Conference on Flexible and Printable Sensors and Systems (FLEPS)*, 2022, pp. 1-4, doi: 10.1109/FLEPS53764.2022.9781564.