

Exfoliated 2D Graphitic-Carbon Nitride Nanosheets as Sensor for Electrochemical Detection of Furazolidone

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The present work demonstrated a facile exfoliation of g-C₃N₄ NSs (E-C₃N₄ NSs) by a sonochemical approach to electrochemical detection of furazolidone (FZD). The structural and morphological characterization of E-C₃N₄ NSs was systematically verified. The results showed that the as-fabricated E-C₃N₄ NSs modified electrode exhibited an exceptional electrocatalytic activity for FZD comparing the bare electrode due to the better catalytic activity, electrical conductivity, distinct structure, high specific surface area, and high carrier mobility. Under optimum experimental parameters, the linear detection range of the E-C₃N₄ NSs-based electrochemical sensor is in a range from 0.002 to 224 µM with a detection limit of 0.0005 µM, which is higher than most reported electrode materials. In addition, the proposed electrode demonstrated strong selectivity and better operational stability toward FZD detection. Interestingly, our proposed electrode was effectively applied to detect FZD in environmental and biological samples with satisfying recovery values. As a result, the E-C₃N₄ NSs are likely to be used in a variety of electrochemical applications for detecting environmental contaminants.

Keywords: Two-dimensional materials, Antibacterial agent, Electrocatalyst, Electrochemical sensor.

1. INTRODUCTION

Furazolidone (FZD) from the family of nitrofurantoin antibiotics is broadly used as an animal growth promoter, antibacterial and antiprotozoal drug [1–3]. However, the low level of FZD residue in the food chain may lead to decreased white blood cells, mutagenesis, carcinogenesis, bacterial resistance, DNA

damage, teratogenic effects, stomach cramps, kidney and liver failure in all living organisms [4–6]. In this respect, the European Union, China, the United States, Australia, and other developed countries excluded using FZD in the production of animal-derived food [7–11]. Despite the restriction, it is routinely illegally administered in ineffective doses, in livestock farms primarily FZD is mixed with animal feed or water as it is low in cost and high in effectiveness [12, 13]. Hence, it's necessary to build sensing systems for sensitively determining FZD in environmental water and food samples to ensure the safety of all living organisms. Currently, many well-known analytical methods like enzyme-linked immunosorbent assay, fluorimetry, electrochemical sensors, surface-enhanced Raman spectroscopy, microemulsion electrokinetic chromatography, lateral flow immunoassay, high-performance liquid chromatography, and chemiluminescence have been used for detection of FZD [14–19]. Among the aforementioned methods, the electrochemical technique has attracted ample attention owing to the numerous merits of simplicity, excellent performance, trace-level detection, low cost, fast, user-friendly, high sensitivity, and portability [20–25].

As renowned, electrocatalyst plays a dynamic role during the electrochemical reaction to increase the catalytic activity. Graphitic-carbon nitride ($g\text{-C}_3\text{N}_4$) belonging to the family of 2D materials emerged as a promising electrocatalyst and has drawn considerable attention recently [26–30]. It's also significant that $g\text{-C}_3\text{N}_4$ is a stable allotrope owed to the occurrence of tri-s-triazine/heptazine ring and layers that are connected by van der Waals forces [31, 32]. Wang *et al.* reported sonochemical exfoliated $g\text{-C}_3\text{N}_4$ nanosheets (NSs) based nanocomposite for electrochemical detection [33]. Their study proved that the sonochemical exfoliated $g\text{-C}_3\text{N}_4$ NSs provide numerous active sites, surface defects, large surface area, interlayer space, and good chemical stability. So, it's encouraged to design electrodes of $g\text{-C}_3\text{N}_4$ NSs with the many advantages rather than the bulk $g\text{-C}_3\text{N}_4$ to enhance catalytic and electrochemical performances. In light of these advantages, we report a facile ultrasonication route to exfoliate $g\text{-C}_3\text{N}_4$ NSs (named E- C_3N_4 NSs) for electrochemical detection of the FZD. The physical characterization of E- C_3N_4 NSs was systematically carried out. The electrochemical measurement revealed that the E- C_3N_4 NSs modified electrode shows robust catalytic activity compared to the bare electrode due to its physicochemical properties. Notably, the E- C_3N_4 NSs-based electrochemical sensor exhibited a low limit of detection, broad linear range, high sensitivity, strong selectivity, and excellent reproducibility towards FZD sensing. Finally, our proposed electrode was effectively applied to ascertain trace amounts of FZD in actual samples with a satisfying recovery rate.

2. EXPERIMENTAL SECTION

2.1 Materials and reagents

Dicyanamide, sulfuric acid, FZD, and other reagents were all purchased from Sigma-Aldrich. Deionized (DI) water is used in preparing all the aqueous solutions. For all the electrochemical sensing measurements phosphate buffer solution (PBS; 0.05 M) is used.

2.2 Synthesis of E-C₃N₄ NSs

The E-C₃N₄ NSs were synthesized following the reported procedure [3]. 3 g of dicyanamide was placed in a single zone tubular furnace and heated to 550 °C under an N₂ atmosphere for 4 h. After that, the as-synthesized product (denoted as “bulk g-C₃N₄”) was precipitated with an adequate amount of DI water/ethanol, collected by centrifugation, and dried at 60 °C overnight.

Next, 1 g of as-prepared bulk material was dispersed in DI water (50 mL) under constant stirring for 15 mins to prepare the homogenous solution. Next, 5 mL of H₂SO₄ was gradually added to the prepared solution. Under ambient temperature, the resultant mixture was located in an ultrasonic bath operating at 60 Hz with the highest output power of 60 W. During the reaction process, the interlayer gap of g-C₃N₄ becomes larger and the thickness of nanosheets was reduced. To make E-C₃N₄ NSs, the material was washed with DI water/ethanol and then left to dry in an oven at 80 °C for 12 hours.

2.3 Instrumentation

The crystal structure was measured by X-Ray Powder Diffraction (XRD) patterns, recorded on Rigaku D/Max 2200 X-ray diffractometer. The surface morphology was observed by Field Emission Scanning Electron Microscope (FE-SEM; FEI Quanta FEG 200) along with Energy-Dispersive X-ray (EDX) spectroscopy and elemental mapping. The electrochemical sensing studies were performed at CHI electrochemical workstation (USA). Under a three-electrode configuration, glassy carbon electrode (GCE), Ag/AgCl (sat. KCl) electrode, and platinum wire was used as working, auxiliary, and reference electrodes, respectively.

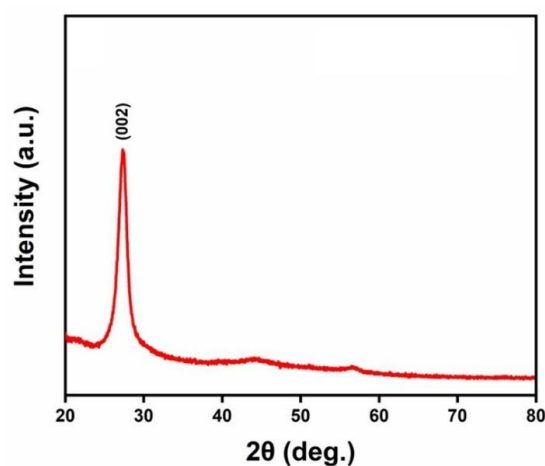


Figure 1. (A) XRD pattern of E-C₃N₄ NSs.

2.4 Electrode Fabrication

Before modification, the bare GCE was polished using alumina slurries and washed off with DI water. A 4 mg of E-C₃N₄ NSs was then dispersed in 1 mL of DI water and treated using ultrasound for

30 mins to form a homogeneous solution. Then, 5.0 μL of dispersion was dropped on the pre-treated GCE and dried under ambient temperature.

3. RESULT AND DISCUSSION

3.1. Physical characterization

The crystal structures of the prepared E-C₃N₄ NSs were examined using XRD measurement. As shown in Fig. 1, two characteristic diffraction peaks at 27.6° are attributed to interfacial packing of π -conjugated C–N heterocycles (002) of E-C₃N₄ NSs [3], respectively. No other impurity characteristic peaks are detected. These XRD results indicate that the E-C₃N₄ NSs are successfully fabricated. The morphologies of the prepared E-C₃N₄ NSs were observed using FE-SEM images at different magnifications as shown in Fig. 2 (A, B). It is seen that the E-C₃N₄ NSs show 2D nanosheets like nanostructures with crumples and wrinkles. The EDX spectrum (Fig. 2C) and elemental mapping (Fig. 2 (D, E)) analysis of E-C₃N₄ NSs authorizes the occurrence of C and N elements within the selected area, which is consistent with the XRD measurement.

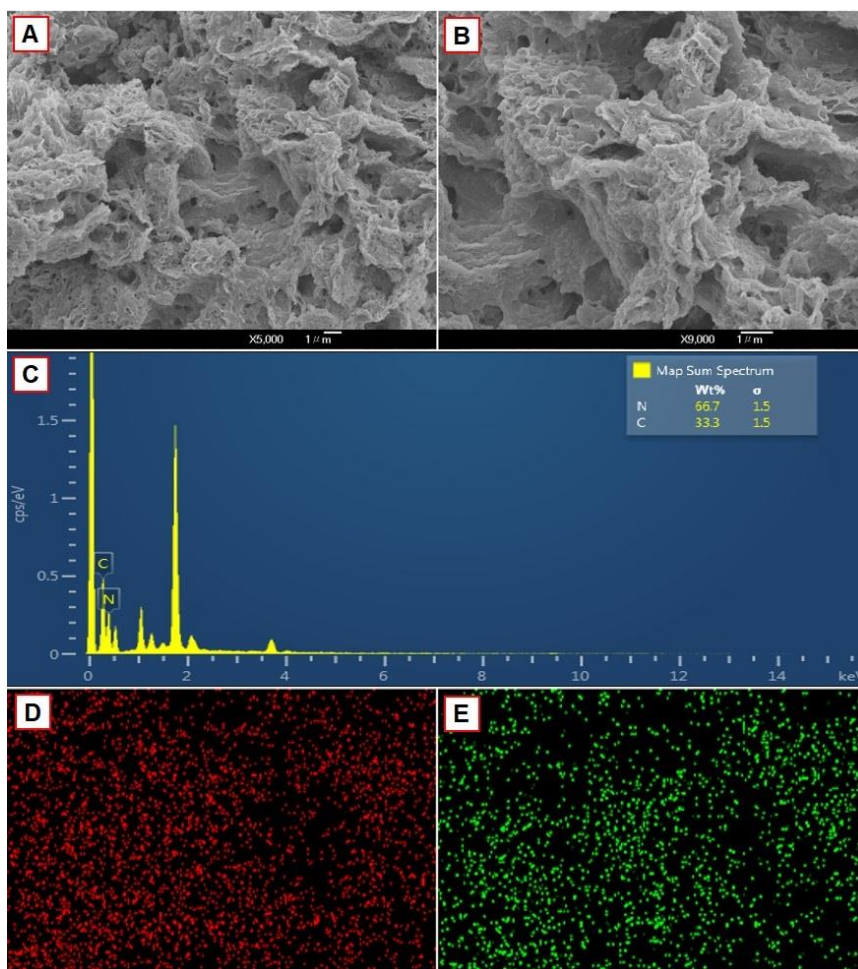


Figure 2. (A, B) FE-SEM images, (C) EDX spectra, and (D, E) elemental mapping of E-C₃N₄ NSs.

3.2 Electrochemical analysis

3.2.1. Electrochemical properties of the electrodes

Electrochemical Impedance Spectroscopy (EIS) technique was used to investigate the intrinsic conductivity of the bare GCE, B-C₃N₄ NSs/GCE, and E-C₃N₄ NSs/GCE in 5 mM [Fe(CN)₆]^{3-/4-} containing 0.5 M KCl (Fig. 3A). The Nyquist plot has been drawn according to the Randles equivalent circuit in the inset of Fig. 3A. The semicircle diameter at high frequency refers to the R_{ct} value on electrodes [1]. The EIS measurement shows the R_{ct} values for the bare GCE, B-C₃N₄/GCE, and E-C₃N₄ NSs/GCE estimated as 611 Ω , 229 Ω , and 96 Ω , respectively. The lesser R_{ct} value of the E-C₃N₄ NSs/GCE represents a high conductivity, which is beneficial for electrocatalytic activity towards FZD detection.

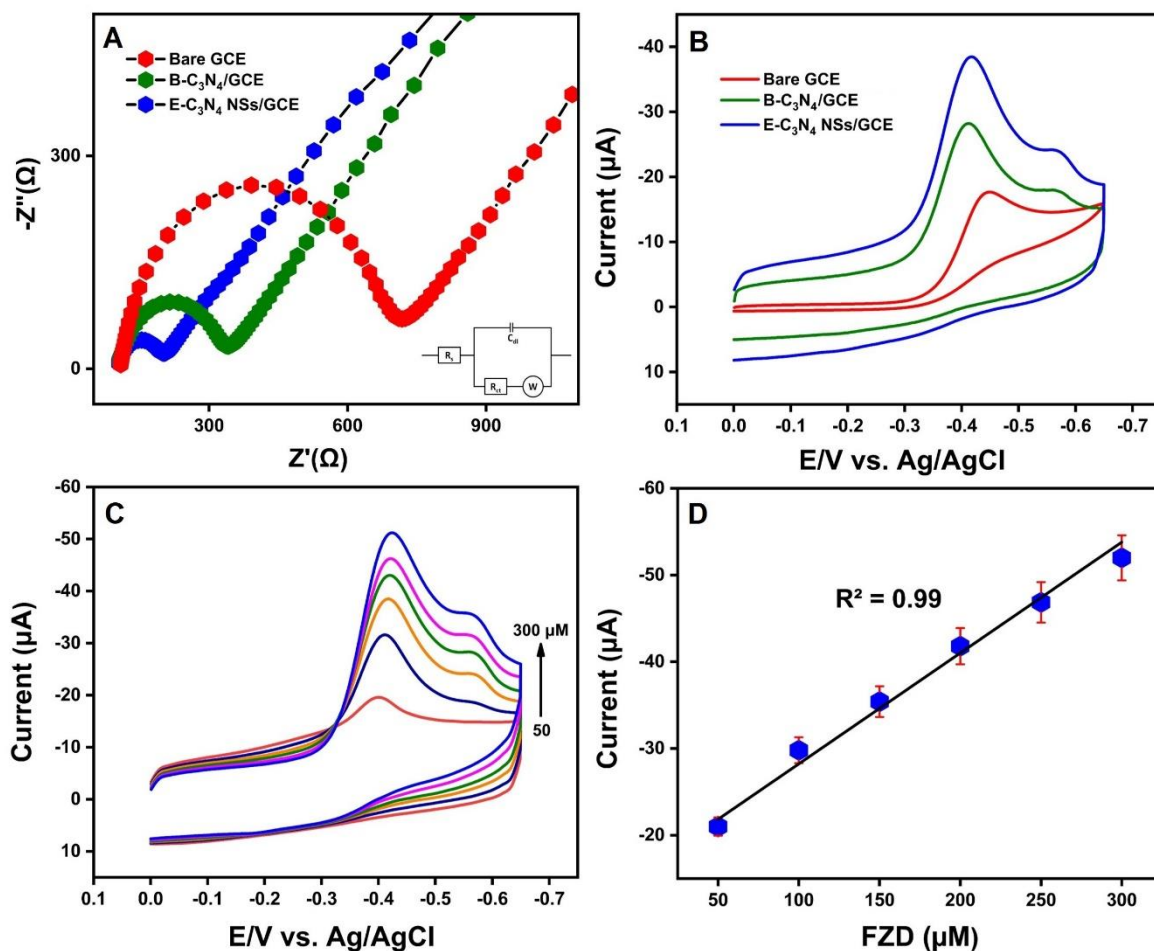


Figure 3. (A) EIS characterizations of different electrodes (Inset: Randle's circuit model). (B) CV responses of various GCEs in 0.05 M PBS (pH 7.0) containing 150 μM FZD. (C) CV responses of E-C₃N₄ NSs/GCE at different concentrations. (D) Linear plot of FZD concentration vs. peak current (μA).

3.2.2 Electrochemical behavior of GCEs

The electrochemical analysis of bare GCE, B-C₃N₄/GCE, and E-C₃N₄ NSs/GCE was investigated using the Cyclic Voltammetry (CV) method in the existence of 150 μ M FZD (Fig. 3B). It is seen that the reduction peak potential was located at -0.44 V with a cathodic current of -17.95 μ A for the bare GCE. The cathodic peak (R₁) is attributed to the four electrons and four protons ($4e^-$, $4H^+$) transfer process of the aromatic nitro group of FZD to hydroxylamine. The Electrochemical Reduction Mechanism of FZD is revealed in Scheme 1 [1–3]. Compared to the bare GCE, the peak current of FZD at B-C₃N₄/GCE increased significantly, reaching -28.5 μ A at -0.412 V, which contributed to the outstanding acceptable properties. When GCE is altered with E-C₃N₄ NSs, the cathodic peak potential shifts in the slight anodic direction of -0.41 V with a peak current of -38.5 μ A. The corresponding cathodic current for FZD at E-C₃N₄ NSs/GCE was 1.35 times and 2.15 times greater than the bare GCE and E-C₃N₄ NSs/GCE due to the better catalytic activity, electrical conductivity, distinct structure, active sites, and high specific surface area. The results suggest that the E-C₃N₄ NSs/GCE has a significant electrocatalytic activity for the reduction of FZD.

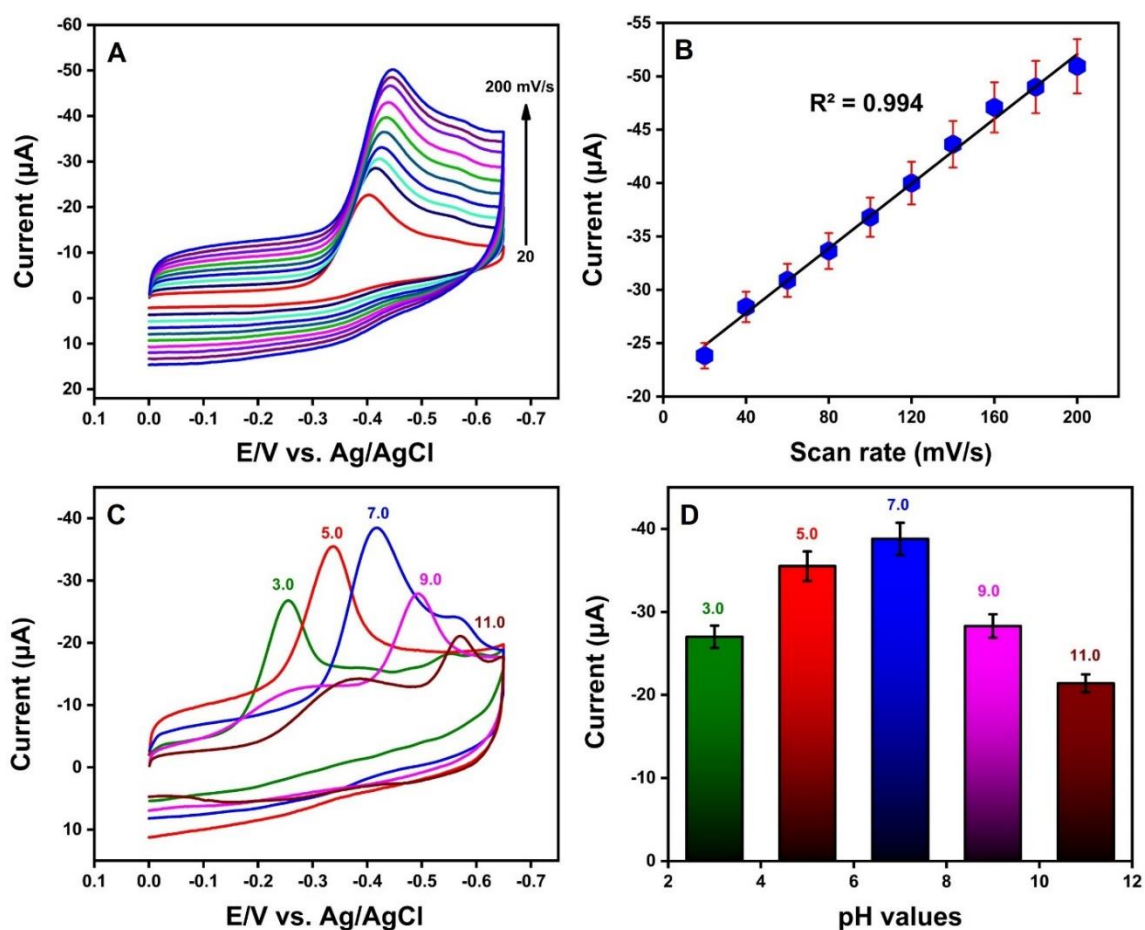
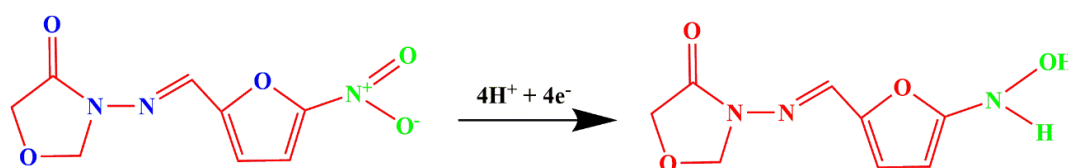


Figure 4. (A) CV responses of E-C₃N₄ NSs/GCE at different scan rates. (B) Linear plot of scan rate vs. peak current (μA). (C) CV responses of E-C₃N₄ NSs/GCE at various pH values. (D) Dependence plot of the peak current on the pH value.

3.2.3 Influence of concentration, scan rate, and pH value

The CV curves of E-C₃N₄ NSs/GCE at different concentration of FZD is exposed in Fig. 3C. The reduction current increases significantly with the increase of FZD concentration from 50 to 300 μM . Notably, the peak current increases linearly with the increasing concentration of FZD (Fig. 3D). The linear regression equation is determined as $I_{\text{pc}} (\mu\text{A}) = -0.1214 [\mu\text{A}/\mu\text{M}] - 16.557$ with a correlation coefficient (R^2) of 0.99. These results reveal that E-C₃N₄ NSs/GCE acted very proficiently towards FZD detection.

The effect of scan rate was studied in presence of 150 μM FZD containing 0.05 M PBS (pH 7.0) using E-C₃N₄ NSs/GCE. Fig. 4A displays that the cathodic peak currents increase with an increase in the scanning rate from 20 to 200 mV/s. The reduction peak current of E-C₃N₄ NSs/GC displays a linear relationship with the different scan rates (Fig. 4B). The corresponding calibration equations can be expressed as $I_{\text{pc}} (\mu\text{A}) = -0.1523 (\text{mV/s}) - 21.677$ with a R^2 of 0.994. It suggests that the electron transfer on E-C₃N₄ NSs/GCE for the electrochemical reduction of FZD is an adsorption-controlled process.



Scheme 1. The electrochemical illustration of FZD sensing.

The study of the pH effect on the E-C₃N₄ NSs/GCE was performed at various pH values (3.0–11.0) of 0.05 M PBS. It is visible that the peak current increased from 3.0 to 4.0 and then gradually decreased (Fig. 4C). Notably, the peak potential gradually shifted with varying pH values, owing to the contribution of protons in the electrochemical reduction process [2, 3]. This relationship between the cathodic peak current and the pH value is illustrated in Fig. 4D. It is observed that a higher peak current appears at pH 7.0. Henceforth, a pH value of 7.0 was chosen as a suitable secondary electrolyte for FZD detection.

3.2.4 Amperometric determination of FZD

The amperometric technique was elected to study the quantitative determination of FZD with E-C₃N₄ NSs/GCE. Fig. 5A displayed the typical amperometric curves of E-C₃N₄ NSs/GCE with successive addition of FZD at an operating potential of -0.41 V in 0.05 M PBS (pH 7.0) under stirring conditions. A well-defined and rapid step-wise current was observed for every addition of FZD in the concentration range from 0.002 to 256 μM . The calibration plot in Fig. 5B shows a linear range of 0.002–224 μM with a R^2 of 0.995. The Limit of Detection (LOD) was calculated as 0.0005 μM ($S/N=3$). The electrochemical detection values of the E-C₃N₄ NSs/GCE were further compared with the previous literature (Table 1).

This contrasting result concluded the performance of the electrochemical sensor of E-C₃N₄ NSs/GCE to detect FZD has a better analytical value than earlier reported electrode materials.

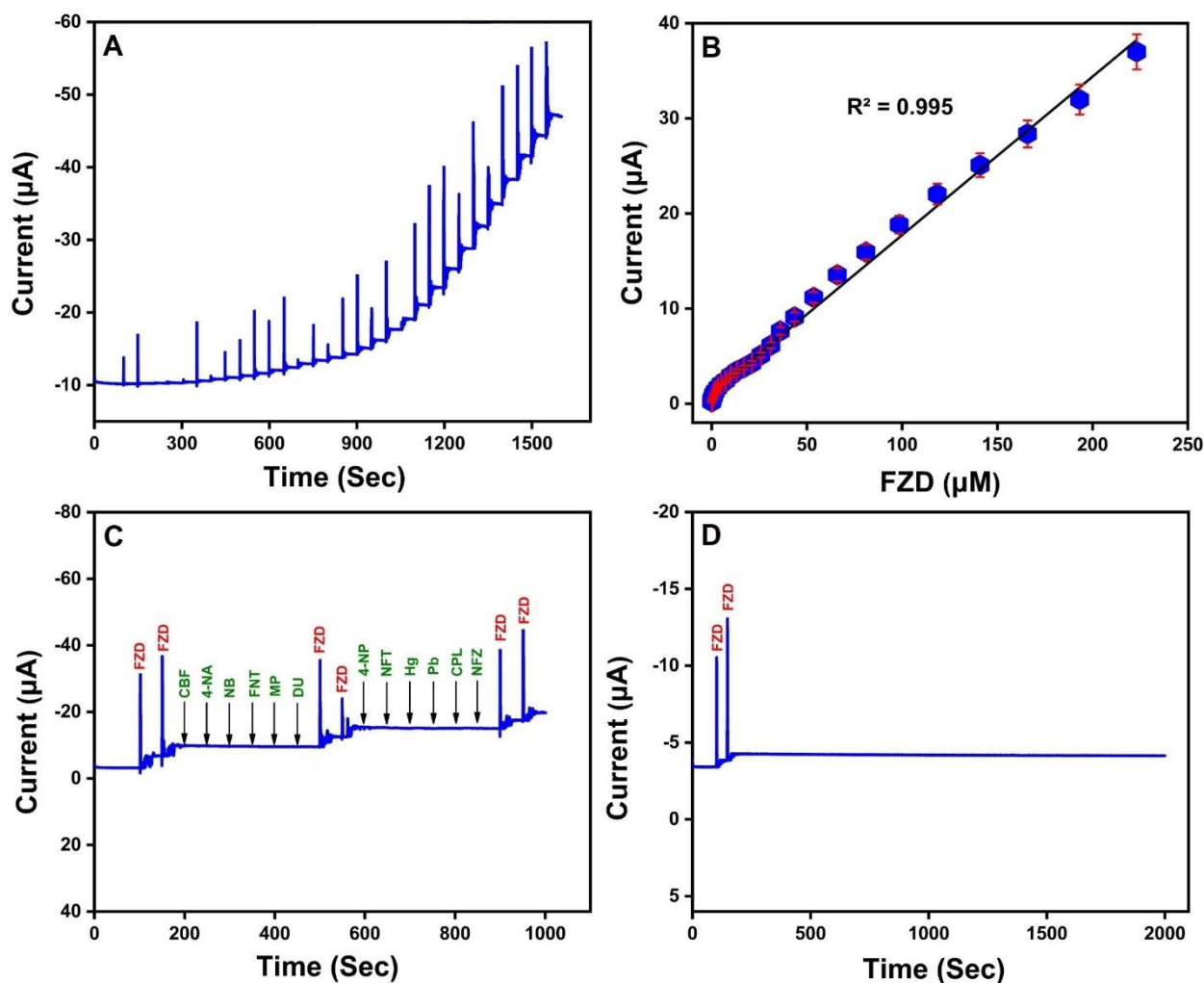


Figure 5. (A) Amperometry responses of E-C₃N₄ NSs/GCE in presence of FZD. (B) The calibration plot of current vs. FZD concentration. (C) Selectivity of E-C₃N₄ NSs/GCE for FZD in the existence of co-interfering compounds. (D) Stability of E-C₃N₄ NSs/GCE toward FZD.

Table 1. Comparison of E-C₃N₄ NSs with other reported sensors for FZD detection.

Electrodes	Methods	Working range (μM)	LOD (μM)	Ref.
ZrP	Amperometry	0.009–339	0.0012	1
h-BN/HNTs	Amperometry	0.009–173.0	0.001	2
VC/g-C ₃ N ₄	Amperometry	0.004–141	0.0005	3
CuS-rGO/g-C ₃ N ₄	DPV	0.1–336.4	0.0108	4
LaVO ₄ /F-BN	Amperometry	0.015–300	0.003	5
CoM/B-C ₃ N ₄	DPV	0.04–408.9	0.00016	7
PAC	Amperometry	0.5–290	0.0005	8
COF@NH ₂ -CNT	DPV	0.2–100	0.0775	13

CB/WC	Amperometry	0.001–1150	0.0006	16
Gr/Au	Amperometry	1–674	0.64	35
BiVO ₄ @MoS ₂	DPV	0.01–14; 14–614	0.0029	36
NiFe ₂ O ₄ /RGO-	DPV	0.1–10; 10–150	0.05	37
RGO	LSV	0.001–2.0, 2.0–10.0	0.0003	38
MWCNT	CV	3–800	2.3	39
NT	DPV	0.01–76	0.004082	40
E-C₃N₄ NSs	Amperometry	0.002–224	0.0005	This Work

3.2.5 Selectivity, operational stability, and reproducibility

The selectivity study is a primary consideration for prospective applications of a newly designed sensor in real-time analysis. The effect of possible interference by various compounds such as carbofuran (CBF), 4-nitroaniline (4-NA), nitrobenzene (NB), fenitrothion (FNT), methyl parathion (MP), diuron (DU), 4-nitrophenol (4-NP), nitrofurantoin (NFT), mercury (Hg), lead (Pb), chloramphenicol (CPL), and nitrofurazone (NFZ), which coexist in the environmental sample along FZD detection was examined by amperometric measurements. Interfering species exhibited negligible responses, as illustrated in Fig. 5C. This result confirms that the fabricated E-C₃N₄ NSs/GCE has the anti-interference ability and excellent selectivity. The operational stability of E-C₃N₄ NSs/GCE was scrutinized using amperometric techniques for the determination of 50 μ M FZD, as exposed in Fig. 5D. The reduction current response of FZD remained at 97% after 2000 s, demonstrating the proposed sensor has good operational stability. The reproducibility of E-C₃N₄ NSs/GCEs was measured by testing five diverse electrodes (Fig. 6 (A, B)). The RSD of the reduction currents for five GCEs is calculated to be 3.01%, confirming good reproducibility of the fabricated E-C₃N₄ NSs/GCEs based electrochemical sensor.

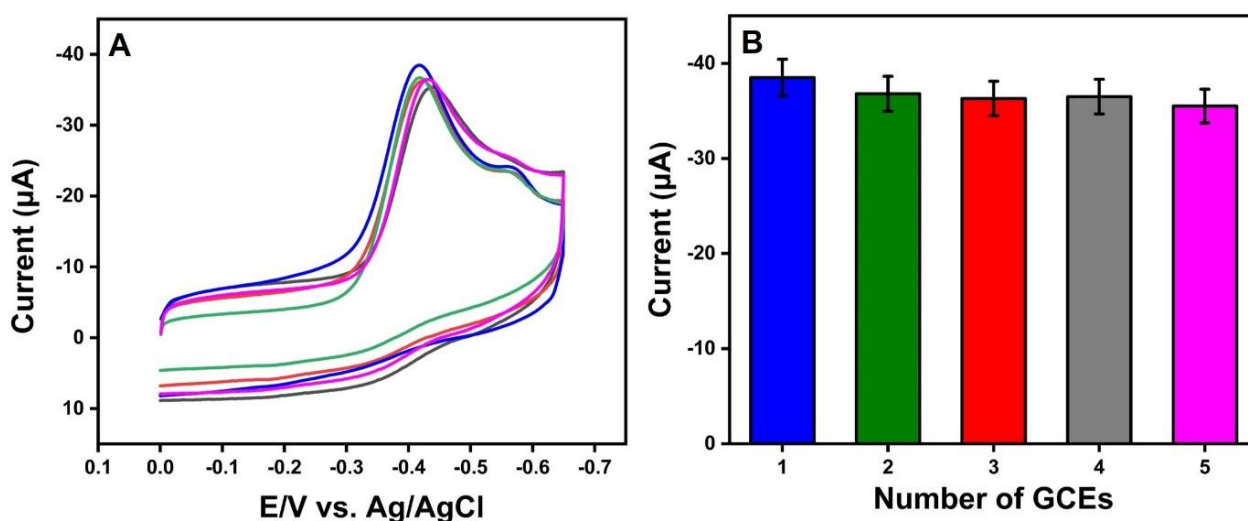


Figure 6. (A) Reproducibility test of various E-C₃N₄ NSs/GCEs for 150 μ M of FZD. (B) The corresponding figure for the reproducibility study.

3.2.6 Real sample analysis

The practical feasibility of the E-C₃N₄ NSs modified electrode was evaluated by detecting FZD in actual samples. The human urine sample is collected from a volunteer from Taiwan. The river water sample is collected from the Xindian River (Taiwan). To remove undesired pollutants, the human urine and water samples were filtered and centrifuged via a Whatman filter paper. The pre-treated samples are free from the FZD and the known content of standard FZD was injected into the pretreated sample. Then, the contents of FZD were determined using the amperometry method via the standard addition method. Fig. 7 (A, B) shows amperometric responses of FZD spiked human urine and river water samples. The results showed that the fabricated E-C₃N₄ NSs sensor has high accuracy and reliability to detect FZD in real-world samples.

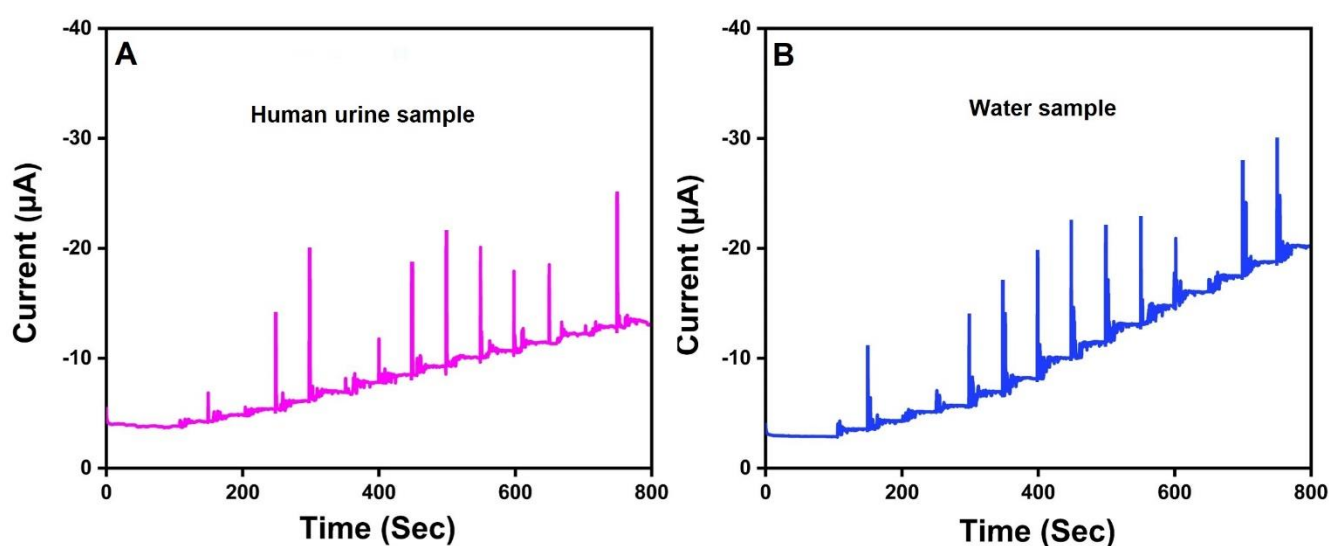


Figure 7. Amperometry responses of (A) human urine and (B) water samples.

4. CONCLUSION

In the present work, E-C₃N₄ NSs have been successfully arranged and applied as an electrochemical sensor for the detection of FZD. The E-C₃N₄ NSs were evaluated by different spectroscopic, and microscopic techniques like XRD, FESEM, EDX, and Elemental Mapping Analysis. The E-C₃N₄ NSs/GCE-based electrochemical sensor displayed an outstanding electrochemical performance towards the detection of FZD compared to the GCE due to the special physicochemical characteristics. The fabricated sensor verified a wide linear range, low LOD, good selectivity, and excellent operational stability for the detection of FZD. The E-C₃N₄ NSs/GCE was successfully utilized toward FZD detection in environmental water samples. Finally, our suggested platform presents an intriguing prospect for determining FZD in human urine and water sample at trace levels.

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