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Electrochemically Modified Poly(dicyandiamide) Electrodes for Detecting Hydrazine in Neutral pH

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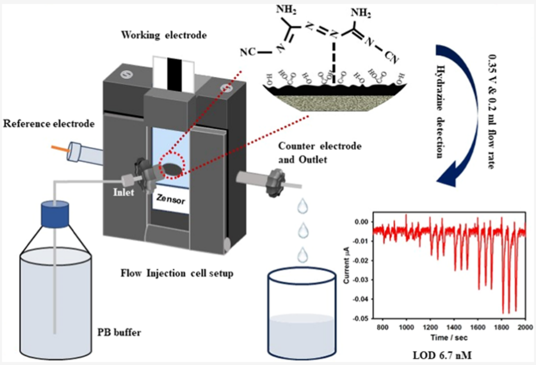
ABSTRACT: A new technique for sensing nanomolar concentrations of hydrazine in water samples is reported. A screen-printed carbon electrode (SPCE) altered using an amine-azo functional group encompassing poly(dicyandiamide) is used in this study. The modified electrode exhibits an enhanced activity toward hydrazine detection at a lower overpotential and broad linear scale between 20 nM and 1 mM, with an accurate sensitivity value of 0.1 nA μm^{-1} cm^{-2}. To the best of our knowledge, poly(dicyandiamide)-modified electrodes exhibit one of the lowest limits of detection for any metal-free electrode that detects 6.7 nM (S/N = 3) of hydrazine. The method established sufficient selectivity and better recoveries. Finally, the poly(dicyandiamide)-modified SPCE* is highly suitable for electrochemical determination of hydrazine in water samples from tap and lake.



INTRODUCTION

Hydrazine, an intense reducing agent as well as a very reactive base, is often used for therapeutic purposes and in photography, pesticides, plant growth regulators, fuel cells, and textile industries. It is also prevalently utilized as a propellant in missile systems, a chemical blowing agent, an emulsifier, a corrosion inhibitor for heating systems, and an oxygen scavenger.[1−7] A prolonged exposure to moderate hydrazine levels can cause adverse health hazards to kidney and liver, weakening of the central nervous system (CNS) as well as brain, and DNA damage, whereas short-time contact can result in giddiness and irritation in the eyes, nose, and also in throat.[5,8,9] Owing to its toxic nature, hydrazine is categorized as a group-B2 human carcinogen.[4,10] Thus, it is essential to establish a precise technique to identify trace levels of hydrazine in both environmental and industrial samples.

There have been multiple detection methods reported for hydrazine determination, such as fluorimetry,[11] spectrophotometry,[12] chromatography techniques,[13,14] chemiluminescence,[15] surface-enhanced Raman spectroscopy,[16] and electrochemical sensors.[17,18] Although the electrochemical sensor method offers one of the simplest and cost-effective approaches with on-field sensing capability, hydrazine oxidation at the bare electrode is poorly catalyzed and requires a high overpotential.[19] Thus, several metal/metal oxide,[20−23] metal complex,[24] and organic mediator[19,25,26]-modified electrodes were developed. The chemically modified electrodes (CMEs) exhibit improved electron-transfer rate, catalytic activity, and lower detection overpotential[27−30] and are continuing to evolve.

Modifiers such as pyrocatechol violet, poly(vinylpyrrolidone), and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) were utilized for the determination of hydrazine.[19,31,32] Multilayer graphene nanobelts (GNBs) for hydrazine sensors are also being explored.[10] Similarly, glassy carbon electrodes modified with gold nanoparticle-decorated mesoporous silica microspheres (GC/Au-MSM),[7] growing hydroxyapatite *in situ* in a chemically reduced graphene oxide composite (HAP-rGO),[18] ZIF-8 on porous nickel films (ZIF-Ni),[33] and glassy carbon electrodes enhanced with cobalt oxide nanocubes combined with reduced graphene oxide on gold nanocomposite[34] are also reported. Despite larger specific surface area as well as

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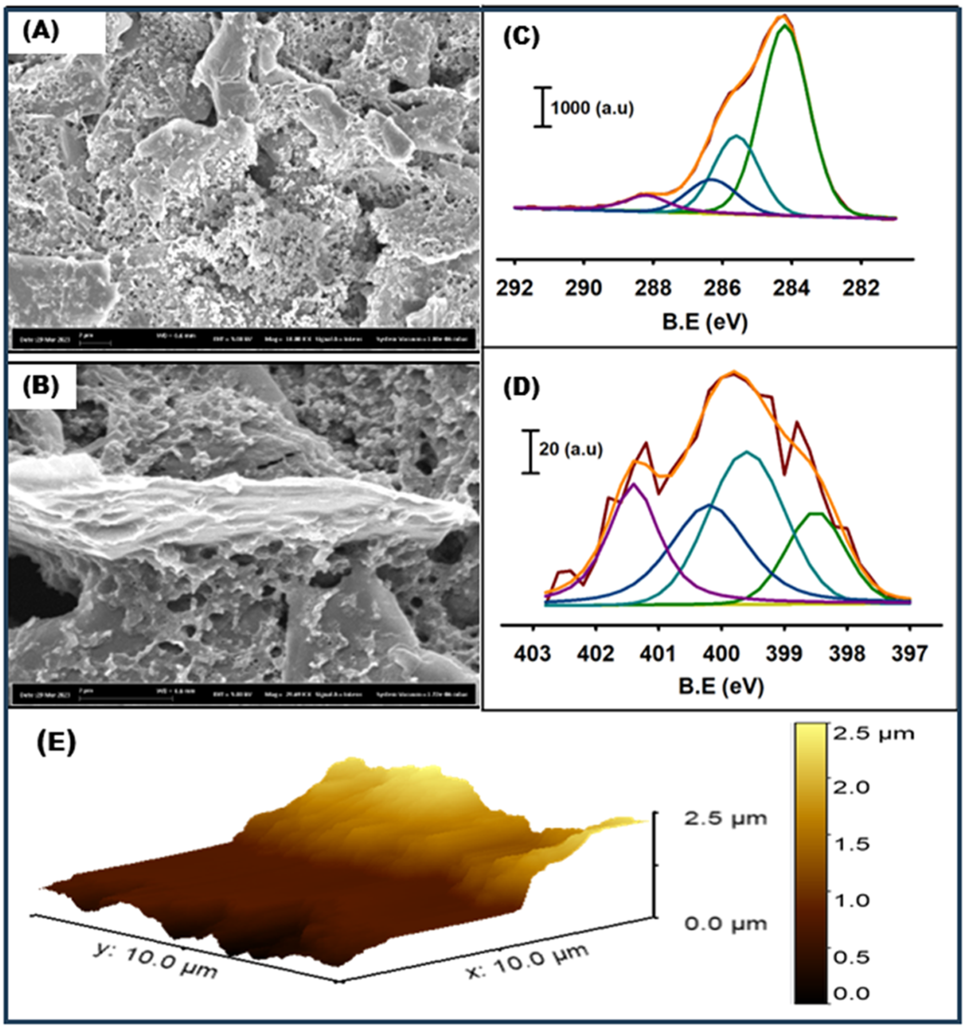

Figure 1. SEM images of the SPCE* (A) and DCD-SPCE* (B) (scale bar: 2 μm). Resolved C 1s of SPCE* (C) and resolved N 1s XPS spectra of DCD-SPCEs* (D). AFM image of the DCD-SPCE* (E).

improved conductivity, some of the systems suffer from long electrode preparation/renovation time, lower sensitivity, and complicated electrode preparation procedures.[35] Therefore, developing sensor systems that are cost-effective with good sensitivity is essential for large-scale applications. Along this line, a robust chemically modified electrode with superior sensitivity and tremendous catalytic activity toward hydrazine detection was evaluated.

In this study, we employed electrogenerated chlorine with a chloride-containing supporting electrolyte to introduce an amine-azo functional group encompassing poly(dicyandiamide) onto a screen-printed carbon electrode (SPCE). This is the first report of in situ electrochemical synthesis of poly(dicyandiamide) on SPCEs*, resulting in the production of DCD-SPCE* specifically for the purpose of hydrazine detection. The poly(dicyandiamide)-modified SPCEs* are utilized to detect a minute amount of hydrazine in water samples. DCD-SPCE* exhibits an enhanced activity in the detection of hydrazine at a lower overpotential showing a specific sensitivity value of 0.1 nA μm^{-1} cm^{-2}. To the best of our knowledge, poly(dicyandiamide) electrodes exhibit one of the lowest limits of detection for any metal-free electrode showing a detection limit value of 6.7 nM.

■ EXPERIMENTAL SECTION

Chemicals and Reagents. 0.1 M Phosphate buffer solution (0.1 M) was produced by mixing 0.1 M Na_2HPO_4 (99.0%, Merck, Germany) with 0.1 M $NaH_2PO_4 \cdot H_2O$ (98.0%, Merck, Germany) and then adjusted to a pH of 7.4 (0.1 M PB). Dicyandiamide was bought from Alfa Aesar, UK (DCD, $C_2H_4N_4$, 99%). Hydrazine was purchased from Sigma-Aldrich (HYZ, N_2H_4, 35%). We utilized analytical grade chemicals for this research, and Milli-Q distilled water from Millipore was employed to prepare aqueous solutions. No extra purification steps were carried out for any of the chemicals used.

Instrumentation and Software. We performed electrochemical experiments using either a CHI-832 electrochemical analyzer from CH Instruments or a Modulab potentiostat from Solartron Analytical, the United Kingdom. These experiments were conducted in a three-electrode cell. We employed a Zeiss Merlin FEG-SEM instrument to conduct scanning electron microscopy (SEM) in this study (Oberkochen, BW, Germany). X-ray photoelectron spectroscopy (XPS) characterizations were accomplished using an OmicronDAR 400. Atomic force microscopy (AFM) is performed in tapping mode with RTESP cantilevers using scan lines of 256 × 256 and a scan speed of 1 Hz (Multimode, Nanoscope IV controller, Bruker).

Electrode Preparation. The disposable SPCE (electrode surface area = 0.196 cm^2) was sourced from Zensor R&D (Taiwan). In these studies, the SPCE underwent electrochemical cleaning through cyclic voltammetry technique ranging from −1.0 to 1.2 V versus Ag/AgCl in 0.1 M PB solution (6 segments). Subsequently, the SPCE was preanodized at 2.0 V, 5 min in 0.1 M PB solution (labeled as SPCE*). Further, the dicyandiamide was polymerized on the SPCE* through a potential cycling procedure spanning +0.2 to +1.55 V in a solution consisting of 0.7 M HCl and 20 mM dicyandiamide (20 segments).

Preparation of Water Samples. Water samples were submitted to an initial filtration process through a 0.25 μm poly(tetrafluoroethylene) (PTFE) membrane filter. Then, they were injected into a 0.1 M PB solution for subsequent electrochemical assessments. The quantity of HYZ in the prepared samples was assessed through our proposed methodology coupled with a standard addition method.

■ RESULTS AND DISCUSSION

Surface Morphology of DCD-SPCE*. SEM images of the SPCE* are depicted in Figure 1A. As can be seen in Figure 1B, the poly DCD-SPCE* surface generated small sponge-like white structures dispersed over the graphite indicating the polymer formation. The DCD-SPCE* surface was also characterized by means of XPS techniques as a confirmation of the presence of the polymeric film. The DCD polymer formation on the SPCE* proceeded through the establishment of an azo-type bond assisted by the in situ electrogenerated chlorine. The XPS characterization was carried out to obtain chemical information on the modified electrode surface. The C 1s spectral analysis revealed the presence of characteristic peaks at 284.2 eV (corresponding to C−C bonds), 285.6 eV (associated with C−OH bonds), 286.3 eV (indicating C−O bonds), and 288.2 eV (attributed to O−C═O bonds). This finding serves as a strong confirmation for the development of oxygen functionalities on the preanodized SPCE electrode surface (Figure 1C). As indicated in Figure 1D, in the deconvoluted N 1s spectra of DCD-SPCE*, distinct peaks are observed at approximately 398.5, 399.6, and 401.4 eV, providing clear signs of imine nitrogen, neutral amine, and carbon−nitrogen−hydrogen (C−N−H) functional groups. Furthermore, the appearance of a peak at nearly 400.2 eV is indicative of the azo-functional group. As the DCD compound does not possess any azo-functional group, it confirms the polymerization through the generation of an azo-bond. The AFM imaging in Figure 1E offers visual confirmation of the surface modification observed in the DCD-SPCE*. The DCD-modified SPCE* exhibits a disorganized morphology with an approximate size of 2.5 μm corresponding to the DCD polymer. The crumpled upper area is primarily a consequence of the increased growth and strong adhesion of the thin film.

Electrochemical Polymerization and Hydrazine Detection. *DCD Polymerization.* To start with, the polymerization of DCD on the SPCE* was carried out in a 0.7 M HCl supporting electrolyte through repeatedly cycling the potential in the range +0.2 to +1.55 V (versus Ag/AgCl) (Figure 2). In this cyclic voltammogram, at around 1.1 V, an oxidation peak emerged, denoting the transformation of dissolved chloride ions into chlorine.[36,37] At roughly 0.8 V, a reduction peak was detected that can be ascribed to the reduction of chlorine produced electrochemically. Apart from these, a couple of redox peaks were observed at ∼0.50 and ∼0.64 V that were associated with the polymerized DCD compound. To confirm this, the SPCE* underwent scanning over the range −0.2 to +0.8 V in a 0.1 M PB solution in the absence of DCD and there were no characteristic results that could be observed to prove the existence of immobilized molecules on the electrode. Since the presence of reversible peaks associated with polymerized DCD, from ∼0.50 to ∼0.64 V, can only be observed in the presence of the HCl supporting electrolyte with pH 1.0 (≤), chloride-containing supporting electrolytes are of essence. Various Cl^--enriched supporting electrolytes like NaCl, KCl, $MgCl_2$, and $CaCl_2$ were utilized upon the polymerization processes. However, no redox peaks were observed under any of these environments similar to our earlier report.[38] Based on the above observation, a potential influence of protonation, which may be essential for the DCD oxidation process, is assumed. Finally, the redox peaks of the oxidized form of the DCD compound could be observed only at pH 1.0 (≤), and the oxidation carried out with different parameters failed to elicit redox response upon repetition. A previous investigation has established that the presence of an acidic pH is essential for stabilizing the radical cation, facilitating the synthesis of the polymer. Thus, a similar mechanism of polymelamine and polyaniline can be attributed in the case of DCD as well.[39,40] In addition, we examined the effect of varied concentration of the HCl electrolyte, ranging between 0.1 and 1.0 M, and observed 0.7 M HCl exhibiting a higher response for hydrazine oxidation.

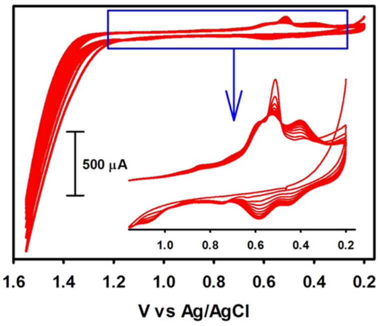

Figure 2. Cyclic voltammogram of DCD polymerization in 0.7 M HCl at pH 1.0.

As previously reported, the electrochemically produced Cl_2 undergoes dissolution in an aqueous medium resulting in $Cl_2(aq)/Cl_3^-/HOCl$ in an aqueous medium.[41] The electrochemically produced Cl_2 can affect the chemical oxidation of the amine performance in DCD to produce chloramine.[42,43] Further, the electro-reduction of chloramine at ∼0.8 V can lead to the formation of a nitrogen-centered radical,[44] and in turn, this nitrogen-centered radical can react with oxygen functional groups at the SPCE* via the covalent bond.[37,45] However, the DCD also has an additional free amine group ($-NH_2$), which can also follow the above-mentioned mechanism to form another nitrogen-centered radical with the help of electrogenerated chlorine. We thus propose that the nitrogen-centered radical can combine with another nitrogen-centered radical of DCD to form a polymer containing −NH−NH− (hydrazo). This assumption is also supported by the above XPS results.

Electrochemical Behavior of Hydrazine. As shown in Figure 3, because of the lack of hydrazine, no specific response was detected at SPCE* (curve A) and DCD-SPCE* (curve C). Figure 3 (curve B) shows the cyclic voltammetric performance

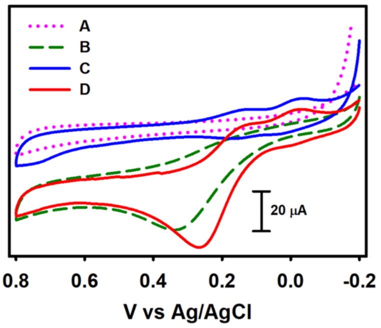

Figure 3. Cyclic voltammetric behavior without and with 1 mM HYZ on SPCE* (A, B) and DCD-SPCE* (C, D).

of hydrazine at SPCE* in 0.1 M PB. The electrochemical detection of hydrazine at SPCE* requires a slightly excess overpotential (~0.4 V) and resulted in a lower current response (curve B). However, the detection of hydrazine at DCD-modified SPCE* exhibited an increased current response with a lower overpotential of ~0.3 V (curve D). As observed, hydrazine is easily involved in the hydrogen-bonding formation (NH···N), onto the DCD-SPCE* surface,[46−47484950] and consequently then triggering the onset potential for sensitive detection of hydrazine through the ECE mechanism.[51−53]

Figure 4A shows the amperometric curves at DCD-SPCE* without (curve a) and with various concentrations (curves b–g), from 100 to 1000 μM, of HYZ. The amperometric curve revealed an orderly increase in anodic current with the HYZ concentration, and a linear relationship was found among the current tested at 25 s with all of the HYZ concentrations (inset of Figure 4 A). Additionally, the diffusion coefficient of hydrazine at DCD-SPCE* in 0.1 M PB was calculated using the Cottrell equation, eq 1.

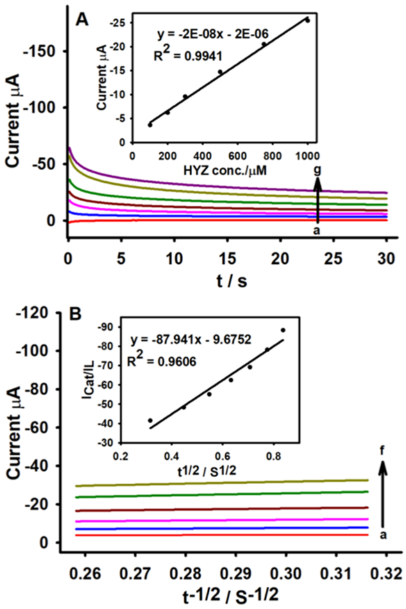

Figure 4. (A) Amperometric response of HYZ: (a) 0 μM, (b) 100 μM, (c) 200 μM, (d) 300 μM, (e) 500 μM, (f) 750 μM, and (g) 1000 μM in 0.1 M PB. Inset: current response at 25 s versus numerous HYZ dilutions. (B) Plots of current response versus $t^{-1/2}$ at numerous HYZ dilutions. Inset suggests the graph of I_{cat}/I_L vs $t^{1/2}$ at 1 mM of HYZ.

$$I = n\pi^{-1/2}t^{-1/2}D^{1/2}FAC \tag{1}$$

Based on amperometry data at intermediate times, a graph of HYZ current vs $Qt^{-1/2}$ is drawn for numerous HYZ dilutions (Figure 4B) and the average diffusion coefficient value is estimated to be 6.5×10^{-6} cm^2 s^{-1}.

The catalytic reaction rate constant (k) is estimated by eq 2:

$$I_{cat}/I_L = (\pi kCt)^{1/2} \tag{2}$$

The slope of the plot I_{cat}/I_L vs $t^{1/2}$ with 1 mM HYZ (inset of Figure 4B) and the calculated "k" was 246069.71 M^{-1} S^{-1}.

Figure 5 shows the performance of the scan rate at peak current of 1.0 mM HYZ in the range 10–200 mV s^{-1} in 0.1 M PB. The peak currents (ip_a) go up linearly with the increasing scan rate. The logarithmic plot of the HYZ oxidation peak response against the scan rate (Figure 5, Inset) yielded a slope of ~0.37, indicating a diffusion control behavior,[51] and the linear regression (eq 3) shown as follows:

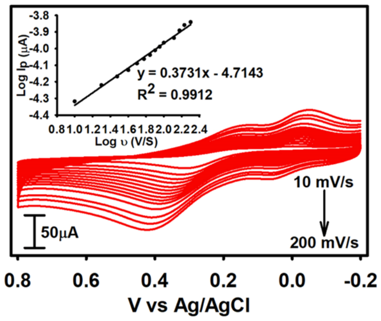

Figure 5. Cyclic voltammograms recorded for DCD-SPCE* at various scan rates, with the solution containing 1.0 mM HYZ in 0.1 M PB at pH 7.4 (a–i: 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, and 150 mV s^{-1}). Inset graph showing the logarithmic plot of scan rate versus peak current.

$$\text{peak: } Ep_a = 0.3731x - 4.7143(R^2 = 0.9912) \tag{3}$$

Figure 6A illustrates the pH analysis of DCD-SPCE* at various pH values between 5.0 and 9.0, with 1 mM HYZ in 0.1 M PB. Observing the data, it becomes evident that as the pH values increase, the oxidation peak potential of HYZ (E_p) shifts to a negative side. The graph depicting the relationship between E_p and pH reveals a linear connection, characterized by a slope of 58 mV/pH as illustrated in Figure 6 B. The system demonstrated Nernstian behavior with the observed slope value closely approximating the predicted value of 59 mV/pH. This alignment suggests an equilibrium between the number of electrons and protons engaged in the reaction. The activity aligns with findings in previous studies,[60] which mentioned the reaction given below for the hydrazine detection:

$$-N = N - + N_2H_4 \rightarrow -HN - NH - + N_2 + 4H^+ + 4e^- \tag{4}$$

The confirmation of accelerating electron transfer of DCD modified on the SPCE and the difference in electrochemical responses of the DCD-SPCE*, SPCE*, and unmodified SPCE were monitored using CV in 5 mM $[Fe(CN)_6]^{3-/4-}$ solution in a 0.1 M KCl electrolyte (Figure 7A). The standard reversible behavior of the Fe^{II}/Fe^{III} redox pair was detected for the DCD-SPCE*, SPCE*, and unmodified SPCE. Importantly, the

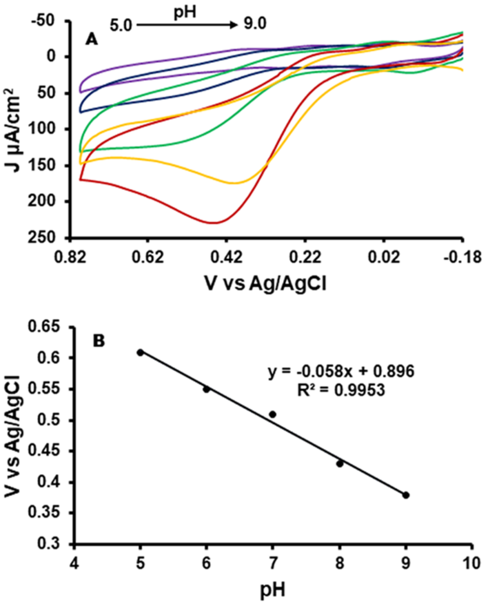

Figure 6. (A) Cyclic voltammograms of DCD-SPCE* at multiple pH in 0.1 M PB (pH 5−9). (B) Plot of pH vs potential.

DCD-SPCE* has the highest redox peak current signal, and SPCE has very low redox peak current signal. Furthermore, a meaningful reduction in the peak-to-peak potential difference (ΔE_p) values between 125 and 80 mV was noticed in SPCE against DCD-SPCE*, correspondingly. This proves that modified DCD-SPCE* is highly electroconductive, stimulates electron transfer, and enhances the active electrode surface area. Electrochemical impedance spectroscopy (EIS) is a reliable practice to check electron-transfer kinetics between heterogeneous interfaces. The electron-transfer process and the active surface area of DCD-SPCE* were additionally estimated using EIS outcomes for the 5 mM $[Fe(CN)_6]^{3-/4-}$ solution in a 0.1 M KCl electrolyte[38] with a Randles equivalent circuit (Figure 7B inset). The Nyquist plot includes two parts: a semicircular segment at higher frequencies that agrees with the charge-transfer resistance (R_{ct}) that influences the electron-transfer step, and a linear segment in a lower frequency range that agrees with the diffusion process. A large half-circle was obtained for unmodified SPCE (548 kΩ), which exhibited considerable electron-transfer hindrance (Figure 7B). The R_{ct} values were found to be 1.02 × 10^{-4} and 2.98 × 10^{-4} kΩ for the SPCE*-DCD and SPCE*, respectively. The DCD-SPCE* was observed with the smallest R_{ct} value (1.02 × 10^{-4} kΩ) when compared with other electrodes. This result suggests that the modification of the SPCE* with DCD could be qualified to the augmentation of both active surface area and conductivity.

Analytical Performance. To further test the analytical utility, a DCD-SPCE* was coupled with a wall-jet electrochemical flow injection analysis (FIA) system to detect and quantify hydrazine. The optimum working potential and the flow rate for hydrazine detection at FIA with 1 mM HYZ were analyzed at various potentials and flow rates at 0.1 M PB in the mobile phase. Finally, we decided to use 0.35 V and 0.2 mL min^{-1} for the HYZ detection. Under the optimized condition, the FIA (Figure 8A,C) results indicated a linear response between 20 nM and 70 µM and also from 100 µM to 1 mM of HYZ in 0.1 M PB with R^2 values of 0.9999 and 0.996 (Figure 8B,D) and a detection limit (LOD) of 6.7 nM. The calculated specific sensitivity of the DCD-SPCE* was 0.1 nA nM^{-1} cm^{-2}.[62] Further, a comparison study based on analytical sensitivity of the DCD-SPCE* with other polymer/metal nanostructure-modified carbon electrodes is presented in Table 1. In addition, the duplicability (n = 6) and consistency (n = 10) of the DCD-SPCEs* were studied using CV and FIA experiments. Relative standard deviation (RSD) values of 1.96 and 0.7 for the electrode−electrode reproducibility and repeatability were obtained, respectively (Figure 9). Results obtained under the dynamic amperometric method of flow injection condition also established a better operational permanence of the electrodes. The plausible electro active interfering materials during hydrazine detection have been investigated using FIA technique in 0.1 M PB (pH 7.4).

As shown in Figure 10, addition of 100 µM hydrazine showed a higher current signal, while injections of 150 µM concentration of interferents like oxalic acid, glucose, lactose, fructose, sucrose, L-arginine, L-tryptophan, Na^+, K^+, ammonium ion, CO_3^{2-}, nitrate ion, Cl^-, SO_4^{2-}, and acetate ion did not show any response. The DCD-SPCE* showed a good tolerance to all of these interfering substances.

Real Sample Analysis. To analyze the capability of the modified electrode toward the deduction of HYZ in environmental samples, lake water and tap water samples were studied.

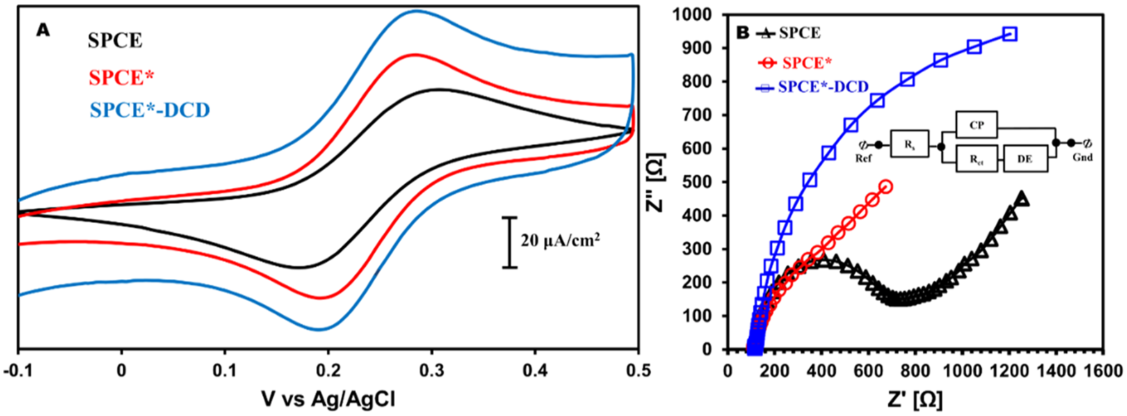

Figure 7. Representative (A) CV of SPCE, SPCE*, & DCD-SPCE* in 5 mM$[Fe(CN)6]^{3-/4-}$ solution in 0.1 M KCl and (B) EIS curves of SPCE, SPCE*, and DCD-SPCE* in 0.1 M KCl solution enriched with 5 mM $[Fe(CN)6]^{3-/4-}$. The inset included within figure (B) presents the circuit model used to fit the EIS data.

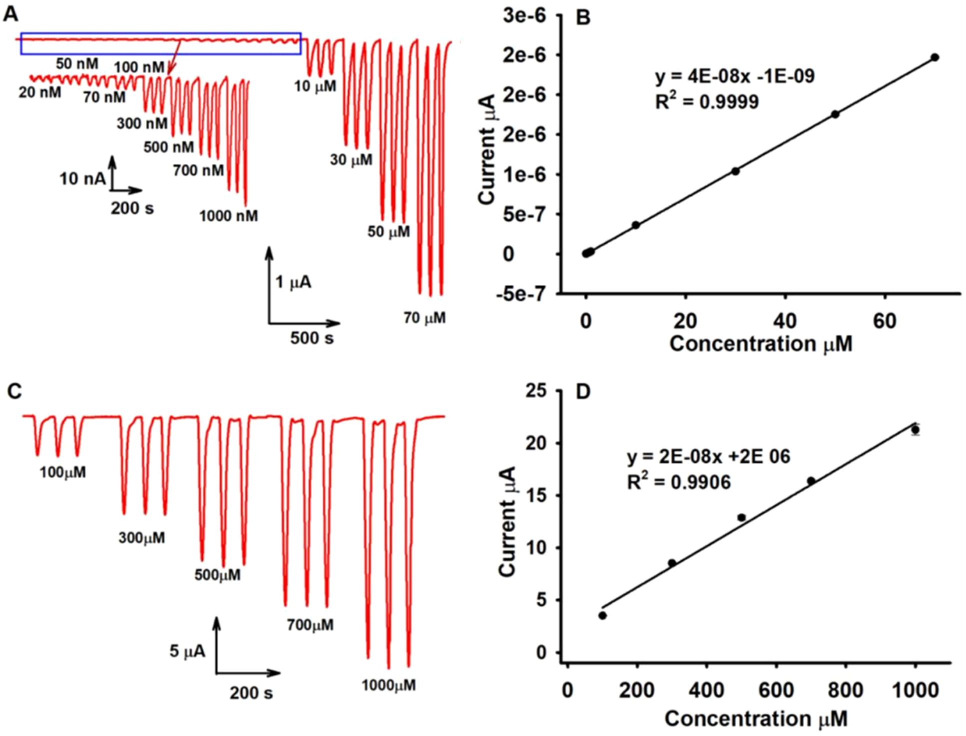

Figure 8. FIA response acquired with increasing strengths of HYZ in 0.1 M PB. Linear response between 20 nM and 70 μM and also from 100 μM to 1 mM (A&C) with R^2 values 0.9999 and 0.9906 (B&D).

Table 1. Comparison Data for the Detection of HYZ with Different HYZ Sensors[a]

s. no	modified electrode	electrochemical method	pH	linear range (μM)	LOD (μM)	references
1	PTh/ZnO/GCE	amperometric	7.4	0.5–48	0.207	54
2	chlorogenic acid/carbon ceramic	amperometric	8.0	0.1–1000	0.02	35
3	HMWCNT/GCE	amperometric	7.0	2.0–122.8	0.68	55
4	*o*-aminophenol/GCE	amperometric	9.0	2.0–20	0.5	56
5	hydroquinone salophen/GCE	cyclic voltammetry	7.5	10–400	1.6	57
6	ErGO/PEDOT:PSS/GCE	amperometric	7.0	0.2–100	0.01	32
7	N-HCSs/SPGE	DPV	7.0	0.02–380	0.007	29
8	PB/CNP/PPy/GC	amperometric		0.75–1653	0.29	58
9	CIT/MCM41/carbon paste	DPV	7.0	0.01–200	0.0033	59
10	AuNPs/CNT/poly(NB)/GCE	amperometric	7.4	1–440	0.33	60
11	AuNPs/CNTs-ErGO/GC	amperometric	7.4	0.3–319	0.065	9
12	ZIF-Ni/ITO	amperometric		2.5–28,000	0.021	33
13	Au-MSM/GC	amperometric	7.0	5–18,000	0.11	7
14	Pt/HNPG	amperometric	7.0	5–6105	1.03	61
15	Pcv/PGE	FIA	9.0	0.25–500	0.08	19
16	DCD-SPCE*	FIA	7.4	0.02–1000	0.0067	this work

[a] GCE, glassy carbon; PTh, polythiophene; HMWCNT, hematoxylin multiwall carbon nanotube; ErGO, electrochemically reduced graphene oxide; PEDOT, poly(3,4-ethylenedioxythiophene); PSS, poly(styrene sulfonate); N-HCSs, nitrogen-doped hollow carbon spheres; SPGE, screen-printed graphite electrode; DPV, differential pulse voltammetry; PB, Prussian blue; CNP/PPy, carbon nanopolyhedra/polypyrrole; CIT, 5-(5-chloro-2,4-dihydroxyphenyl)imidazo[4,5-*d*] [1,3]thiazin-7(3*H*)-one; MCM-41, mesoporous material based on silica; AuNPs, gold nanoparticles; poly(NB), poly(Nile blue); CNT, carbon nanotube; ZIF-Ni, zeolitic imidazolate framework 8 (ZIF-8) and porous nickel films; Au, gold nanoparticles; MSM, mesoporous silica microspheres; Pt, platinum nanoparticles; HNPG, highly surface-roughened nanoporous gold electrode; PGE, pencil graphite electrode; Pcv, pyrocatechol violet.

Because significant HYZ was unable to be detected in the water samples, quantifiable amounts of HYZ were mixed in different water samples and a standard addition method was further adopted to ascertain the recovery values. The data are presented in Table 2. The recovery values fall between 97.2 and 103.7% with a maximum RSD of 3.88 (n = 3). The calculated recovery and RSD validate that the suggested method is appropriate for efficient hydrazine detection in tap and lake water.

■ CONCLUSIONS

The DCD-SPCE* has been demonstrated as a facile technique for the electrochemical detection of HYZ under decreasing overpotential (~0.3 V vs Ag/AgCl) in neutral medium (0.1 M, pH 7.4 PB). The presence of an azo moiety assisted the

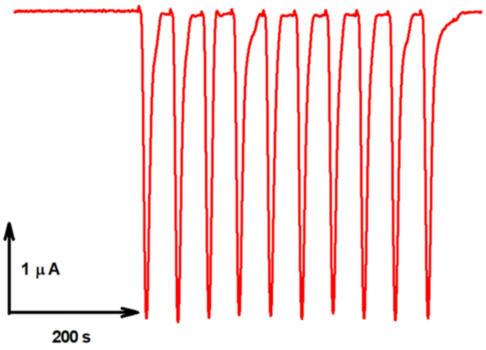

Figure 9. FIA response was derived from a sequence of ten injections, each consisting of 100 μM HYZ into a 0.1 M PB.

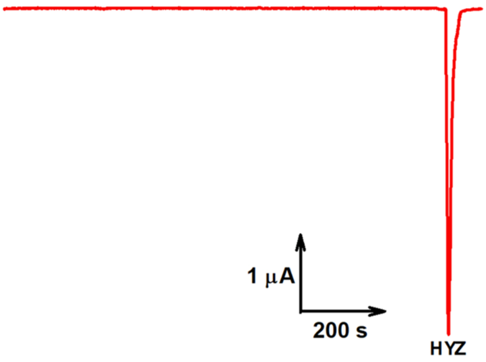

Figure 10. FIA response for injection of 150 μM of interferents along with 100 μM HYZ in 0.1 M PB, pH 7.4.

Table 2. Real Sample Analysis Data of HYZ

samples	added (nM)	detected (nM)	recovery (%)	RSD (%)
tap water	50.0	51.10	101.1	3.53
	100.0	98.70	98.7	3.88
	500.0	498.20	98.2	3.30
	1000.00	1000.50	100.5	0.58
	10000.00	10002.80	102.8	0.42
lake water	50.0	53.70	103.7	3.27
	100.0	100.80	100.8	2.38
	500.0	498.40	98.4	3.77
	1000.00	997.20	97.2	1.24
	10000.00	9997.90	97.9	0.82

electrocatalytic oxidation of HYZ to lower the overpotential, and the existence of other nitrogen functionalities facilitated the hydrogen bonding between the electrode surface and the analyte to improve the sensitivity. The modified DCD-SPCE* exhibited excellent analytical utility and good recoveries for the hydrazine detection in the environmental water samples, making it highly suitable for the detection of hydrazine in environmental water from the tap and lake.

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