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A Green Approach to the Synthesis of Well-structured Prussian Blue Cubes for the Effective Electrocatalytic Reduction of Antiprotozoal Agent Coccidiostat Nicarbazin

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Abstract: For the first time, a robust electrochemical sensor to detect the coccidiostat nicarbazin (NCZ) is developed through the green synthesis of Prussian blue cubes from Volvariella volvacea (paddy straw mushroom) extract. Recently, numerous articles were reported about the issue that the prophylactic drugs were injected excessively as a feed additive for fattening the chickens in short period. It is a significant concern that the level of coccidiostat NCZ exceeds the residue limits in the tissues of the meat; mainly, in chicken and eggs. Therefore, it is crucial to develop a sensitive, reproducible and long-lasting sensor for the real-time detection of NCZ. Thus, we have generated an electrochemical sensor through the economic screen-printed carbon electrode (SPCE) modification method. Eco-friendly Prussian blue cubes are fabricated on the carbon film of SPCE. As a result, the modified electrode showed exceptional electrocatalytic ability towards NCZ and the reduction peak currents are correlated to the concentrations of NCZ. It retains the more extensive working range between 1.25×10^{-7} to 1.53×10^{-3} mol L^{-1}, and it possesses a very low limit of detection as well as the appreciable sensitivity. This method is successfully applied to the recognition of NCZ in the samples of chicken meat and eggs.

Keywords: Prussian blue cubes · Modified electrode · Anti-infective drug · Coccidiostat · Nicarbazin, Biosensors, Biosynthesis

1 Introduction

Coccidiosis [1–3], a parasitic syndrome initiated by coccidian protozoa [4,5], which stimulates weight loss and various intestinal disorders in the cattle. Therefore, the coccidiostats [6,7] were introduced, which were the collection of chemical compounds that could perform as antiprotozoal agents to prevent and treat these contagious diseases affecting mainly poultry, and which is associated with warm and humid conditions, as can be found on poultry farms [8,9]. At the same time, the excess dosage of coccidiostats leads to significant threats to the cattle [10,11]. Among the coccidiostats, nicarbazin [12,13] is one of the traditional anti-protozoal agents which is used till date. Recent reports declare that objectionable levels of nicarbazin residues found in the tissues of the chickens [14–16]. The apparent reason for this massive issue is the excessive addition of prophylactic drugs as a feed additive for fattening the chickens in a shorter period. In recent times, few articles reported about the effects of nicarbazin [17,18]; among the reports, few states that nicarbazin can act as a reproduction inhibitor and it also decreases the hatchability of eggs [19,20]. Therefore, constructing a cheap [21], effective [22] and sensitive device [23] for the real-time detection and quantification of NCZ creates great interest among the researchers.

Prussian blue (PB), the octahedral metal hexacyanoferrates with cubic lattice structure gained its extensive consideration in the field of electrochemical sensors owing to its exceptional electron transference [24,25], catalytic property [26] and mainly, due to it's distinguished conductive and magnetic properties [27,28], it has been widely used in super capacitors [29], batteries [30], storage devices [31,32] and recently in hydrogen storage [33,34] applications. In spite of holding the cyanide anions in its structure, it is non-toxic [35]. Thus, we have synthesized PB cubes eco-friendly through the extraction of Volvariella volvacea (paddy straw mushroom), which reduces $K_3[Fe(CN)_6]$ efficiently, as elucidated in Scheme 2. Though the studies on this extract are limited in literature, Ruixue Chen et al. synthesized PB cubes through the

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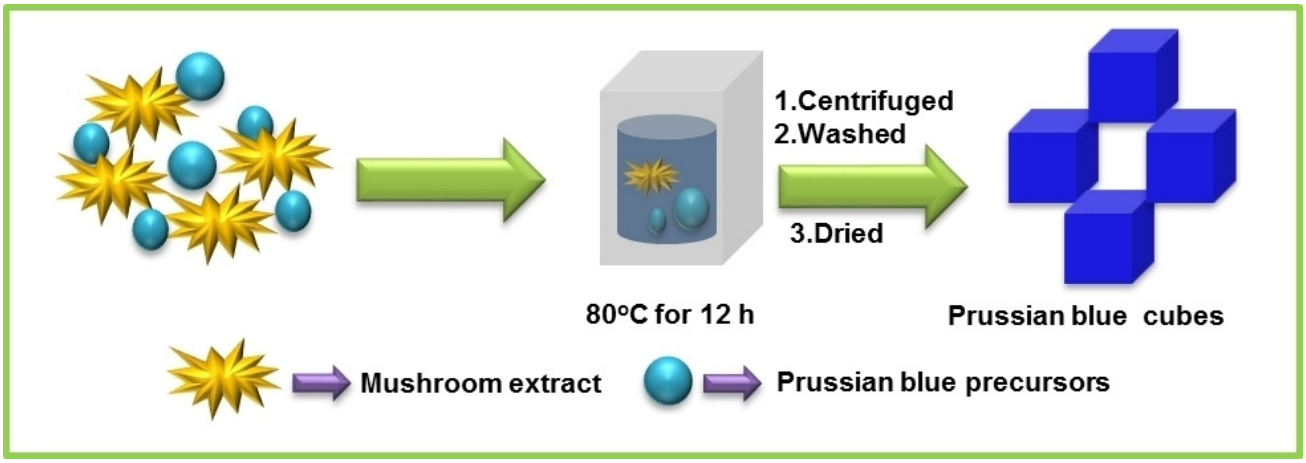
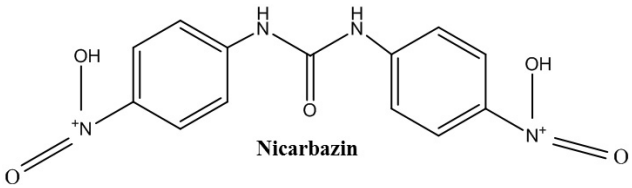


Scheme 1. Preparation method of Prussian blue cubes.

mushroom extract, hardly; however, they have not achieved well-structured PB cubes [36].

In this article, we reported the one-pot synthesis of well-structured PB cubes by the green approach and the prepared cubes are employed for the sensitive detection of nicarbazin. Previously, several bulky techniques like high-performance liquid chromatography [37], liquid chromatography with Tandem Mass Spectrometry [38], etc., were applied for the determination of NCZ. For the first time, the prophylactic drug nicarbazin is detected and quantified accurately by the simple electrochemical method. The PB cubes film modified screen-printed carbon electrode (SPCE) revealed higher electrochemically active surface area, outstanding electrocatalytic facility and offered extraordinary sensitivity towards NCZ.



Nicarbazin

2 Experimental

2.1 Materials and Instrumentations

Potassium hexacyanoferrate(II), polyvinylpyrrolidone (PVP, K30) were purchased and used as received. All the reagents taken are at its best grade for analysis and used without any further purification. The buffer solutions consumed for the electrochemical studies are 0.1 M phosphate buffer (PB). The preparation methods of buffer solutions, chemical purchases, and instrumentation techniques are detailed in the supplementary data (S1).

2.2 Preparation of Mushroom Extract

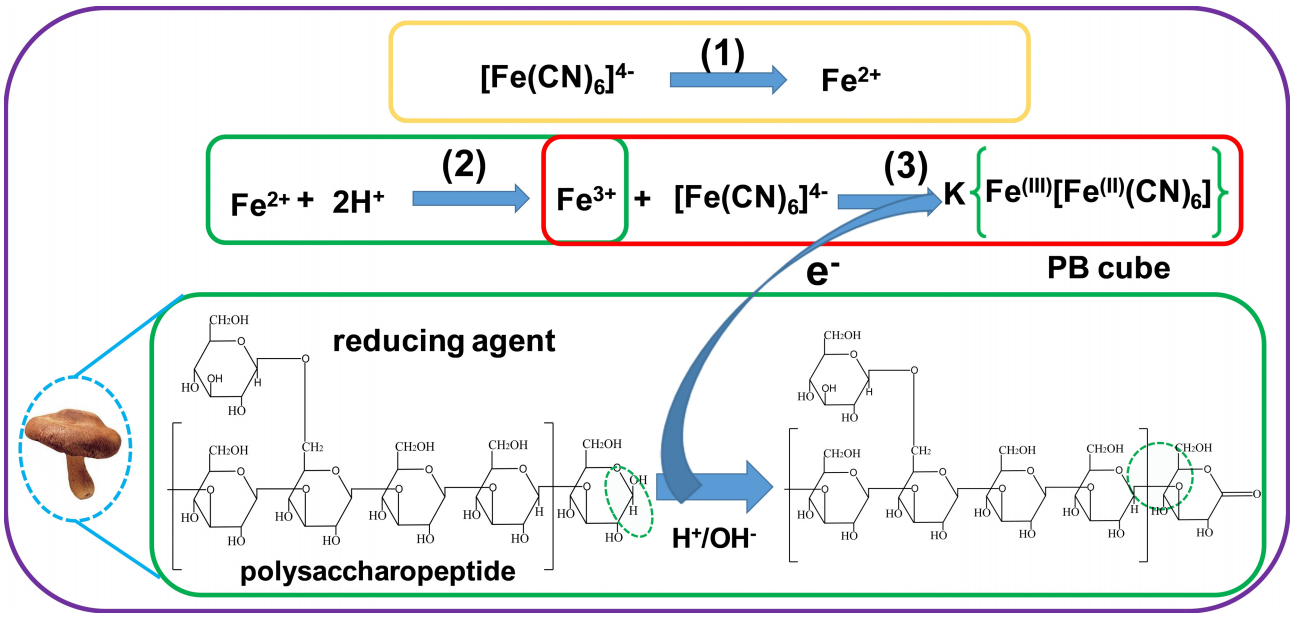
In agreement with the literature [36,39], Fresh Volvariella volvacea (paddy straw mushroom) was purchased from RT-MART, Taiwan. Washed several times with deionized water to clean up the impurities on the surface and chopped into small pieces. Then, the chopped mushrooms were weighed (70 g) and taken in a sterilized borosilicate beaker (200 ml) occupied with distilled water (150 ml) and heated at 80 °C for 3 h, as illustrated in Scheme 1. Finally, the oily syrup like filtrate was taken, cooled and used as an active reducing agent for further reactions.

2.3 Synthesis of PB Cubes

Initially, 8.2 g of polyvinylpyrrolidone (PVP, K30) was dissolved in 30 ml of 5 mM potassium hexacyanoferrate (II) (pH 1), then 20 ml of mushroom extract (pH 1) was added slowly under magnetic stirring. Then, the solution was taken into a 100 mL Teflon bomb. Finally, the autoclave was sealed and maintained at 80 °C for 12 h. The gotten precipitate is wisely separated and washed with deionized water and ethanol, then dried under a vacuum drier at ambient room temperature.

2.4 Fabrication of PB Cubes Modified Electrode

The active surface area of the screen-printed carbon electrode was pre-cleaned by sweeping in the range between −1.0 V and 1.2 V (vs. Ag/AgCl), in pH 5 (0.1 M PB). Next, 8 µl PB cubes dispersion (1 mg mL^{-1}) in ethanol was drop cast on SPCE and dried at room temperature.



Scheme 2. Growth mechanism of PB cubes.

3 Results and Discussions

3.1 Formation of PB Cubes

The reduction of $K_3[Fe(CN)_6]$ by the Volvariella volvacea extract approaches the green synthesis of PB cubes. Jian Cui et al. reported that the mushroom extracts encompasses polysaccharopeptides [40]. Therefore, these reducing sugars in the extract play a substantial role in $K_3[Fe(CN)_6]$ reduction. Due to the high stability constant ($K_s = 1.0 \times 10^{42}$) of $[Fe(CN)_6]^{3-}$, it turns highly stable in neutral solutions. However, it gradually dissociates in acidic medium, tends to produce Fe^{3+}cations. As a final point, the PB cubes are obtained as the result of the reaction between Fe^{3+}cations and $[Fe(CN)_6]^{3-}$ anions as shown in Scheme 2. PVP can assist as a growth modifier, surface stabilizer, and particle dispersant. So, its role depends on the synthetic conditions. Herein, the PVP, K30 efficiently covers the PB cubes as a surface stabilizer in the reaction medium. Therefore, no noticeable aggregation or flocculation is detected in the dispersion because PVP stably stabilizes the obtained PB cubes.

3.2 Morphological and Elemental Characterizations

(Figure 1A–B**)** Exposed the FE-SEM images of PB cubes and that clearly shows the formation of uncountable cubes. The inset of (Figure 1A) showed unexpected crystallinity of individual cube and the cube sizes are ranged in micrometer. (Figure 1C), EDX profile of the Prussian blue cubes exposes existing elements in the synthesized material.

3.3 PXRD and FT-IR

(Figure 2A) Displays the PXRD pattern of synthesized PB Cubes. The material exhibited peaks at 17.6° (200), 24.9° (220), 31.8° (222), 35° (400), 38.8° (420), 42.1° (422), 50.2° (440), 54.7° (442), 57.8° (662), in agreement with standard pattern of Prussian blue (JCPDS 01-073-0687). Gotten PXRD pattern correlates well with that in the literature [41]. Henceforth, the formation of crystalline PB cubes was confirmed. For examining the functional groups, FT-IR spectra of PB cubes was studied (Figure 2B). The spectrum of PB cubes exhibited an absorption band at 2079 cm^{-1}, which is related to the CN functional group ascending from the water responses near 3400 and 1590 cm^{-1} related with H–O–H bend and O–H stretch, respectively. In the far-infrared region, 509 cm^{-1} associated with Fe–C–N–Fe bending modes determines the characteristics of PB MCs. The obtained results are similar to the previous literature [42]. Therefore, the functional groups of crystalline PB cubes are confirmed.

3.4 Impedance Study on PB/SPCE

(Figure 2C) Displays EIS attained at bare SPCE (a), PB/SPCE (b) in 0.1 M KCl comprising 5 mM $Fe(CN)_6^{3-/4-}$. The experimental data acquired by Randles equivalent circuit model (inset), Where, R_{ct}, R_s, Z_w, and C_{dl} were portraying charge transmission resistance, electrolyte resistance, Warburg impedance and double layer capacitance, respectively. The subsequent order indicates the diameter of semicircles (i.e., R_{ct}); Bare SPCE (509 Ω) > PB/SPCE (180.57 Ω). Provided results show the lower resistance at PB cubes over other electrodes.

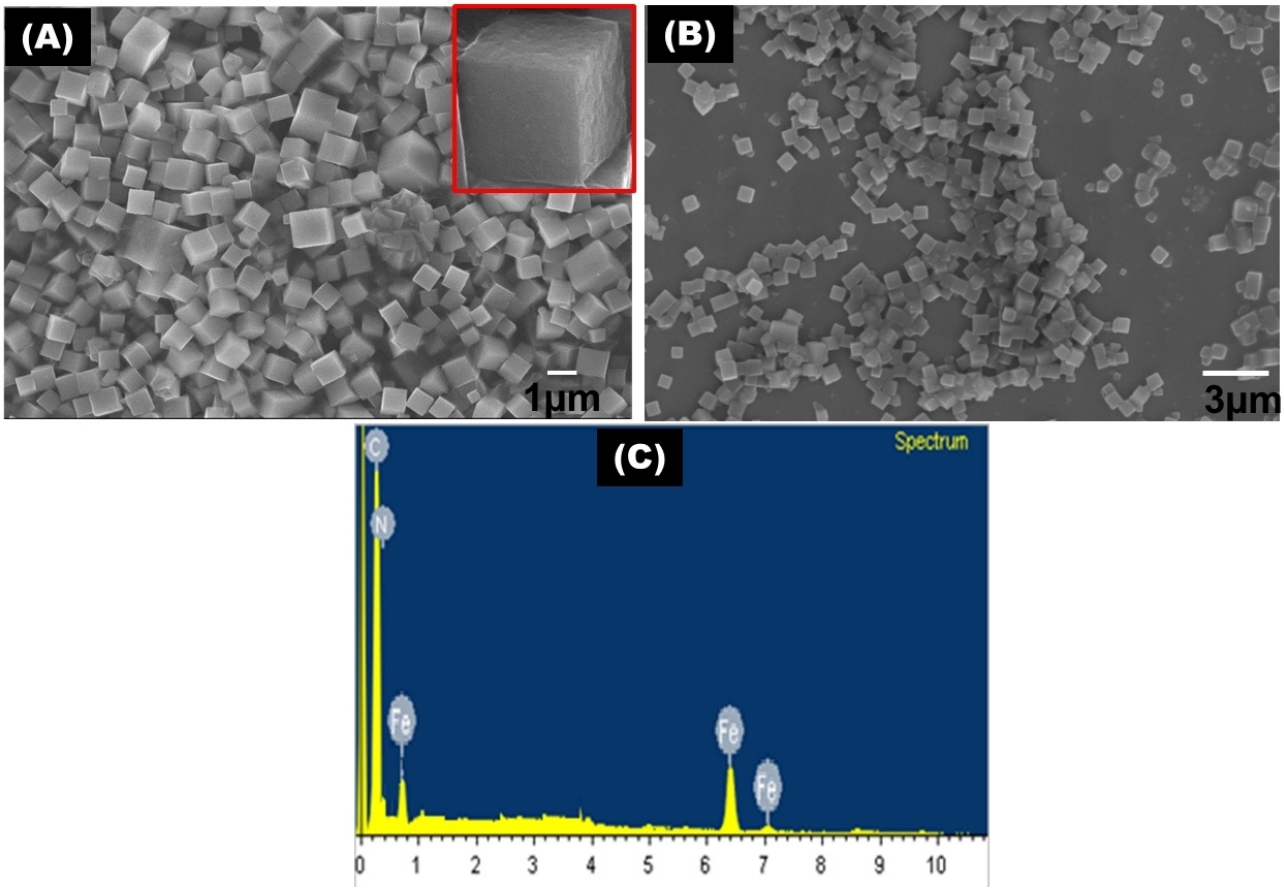


Fig. 1. (A, B) FE-SEM images, and (C) EDX profile of Prussian blue cubes.

3.5 Electrocatalyzing Ability of PB/SPCE towards NCZ

The CVs obtained at unmodified SPCE (a), PB/SPCE (c) in pH 5 containing 25 μM NCZ at the scan rate of 50 mV s^{-1} between the potential range of 0.4 and −1.0 V is demonstrated in (Figure 3A). In the dashed line (b) is the blank of the PB/SPCE obtained without NCZ in pH 5 at the scan rate of 50 mV s^{-1}. The PB/SPCE displayed greater electrocatalytic capability and rapid electron transmissions as revealed by extremely improved cathodic peak currents at minimized over-potential. The peak current acquired at PB/SPCE was 8.3 fold higher than those achieved at bare SPCE. (Figure 3B) Presents the CVs obtained at PB/SPCE in Phosphate buffer (pH 5.0) headed for increasing NCZ concentrations. The cathodic peak current increases as the increase in the concentrations of NCZ (inset). The reduction peak current was periodically improved as the increase in scan rate, which unveiled the signifying electrocatalytic property of the diffusion-controlled electrocatalytic process (Figure 3C). The graphically plotted outcomes between the reduction peak current and the square root of scan rate confirm the linearity, as shown in (Figure 3D). The pH influence on the electrocatalytic response towards NCZ was examined. The reduction peak currents fluctuated as the pH buffers were altered and finally, touched maxima at pH 5, and charted diminished trend at basic pH buffers (Figure S1).

3.6 Amperometric Determination of NCZ

(Figure 4A) shows the amperometric *i-t* curve acquired for PB cubes adapted electrode upon subsequent additions of 0.125, 6, 12, 20, 60, and 90 μM of NCZ into pH 5 at periodical intermissions of 50 sec ($E_{app} = -0.79$ V, vs. Ag/AgCl). Steady, and stable results were witnessed on each addition, and the resulting current improved linearly as the NCZ concentrations increased (Figure 4B). Therefore, the linear range is between 1.25×10^{-7} to 1.53×10^{-3} mol L^{-1}. The limit of detection was 5.8×10^{-8} mol L^{-1}, and the sensitivity reached is 2847 μA/mM/cm^2. The obtained amperometric results are compared with the previously reported methodologies in (Table S1)

3.7 Selectivity towards NCZ

The selectivity towards NCZ is measured by the amperometric studies with the co-existence of interfering components, which were mostly given to the cattle as a feed additive and also as a coccidiostat. (Figure 5B) shows the selective amperometric responses of PB cubes modified electrode to 5 μM of NCZ (a), 50 μM of Sulfadiazine (b),

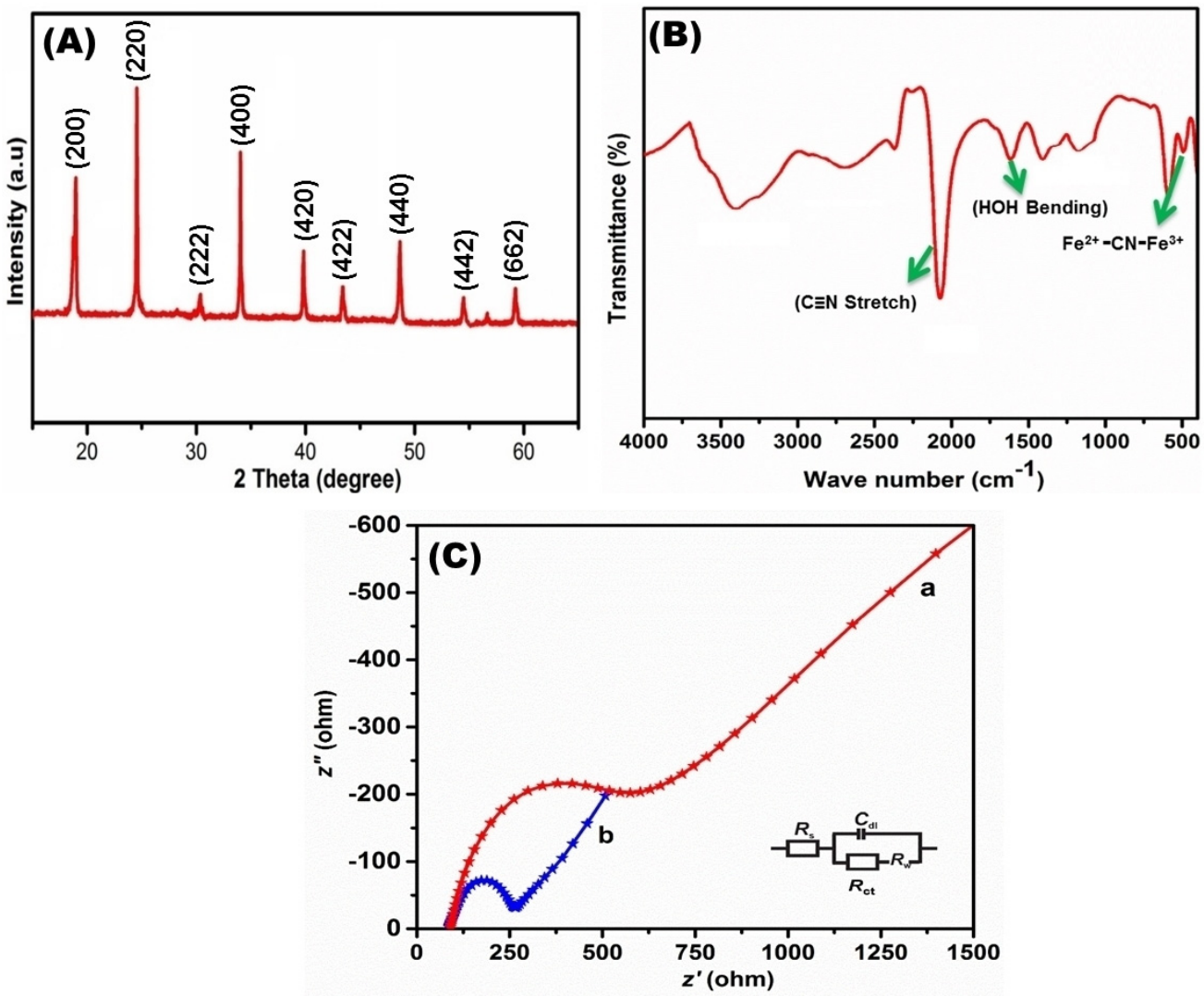


Fig. 2. (A) PXRD pattern, (B) FT-IR spectrum of Prussian blue cubes, and (C) EIS curves of bare SPCE (a), PB/SPCE (b) raised in 0.1 M KCl containing 5 mM $Fe(CN)_6^{3-/4-}$. Inset: Randles equivalent circuit.

Amprolium (c), Diclazuril (d), Sulfacetamide (e), Sulfaguanidine (f), D-penicillamine (g), Doxycycline (h), Clazuril (i), and Ponazuril (j). As a final point, the system selectively responded towards NCZ in the buffer, which was influenced by the mixture of interfering chemicals.

3.8 Reproducibility and Durability

The prepared electrode's responses were examined on a daily basis to observe the wearing ability. But, the sensor maintained 98.4 % of its first response even after a month although used continuously, authenticated the moral wearing consistency of the proposed electrode. On examining the reproducibility, CVs are obtained from 5 separate PB/SPCEs in the buffer holding 25 μM NCZ; the obtained relative standard deviation was 2.6 %. Stability plot (Figure 5A) for the electrode is plotted as its sequential usage for one month. The CV responses of PB/SPCE towards 25 μM NCZ in phosphate buffer (pH 5.0) is monitored every day (Figure S4); when it was not in use, it was stored in a refrigerator at 5 °C.

3.9 Real Sample Analysis (Chicken Meat, and Egg Sample)

The applied practicality of the system is verified in the samples of chicken meat and egg. With the intention of quantifying the NCZ in chicken meat samples, fresh meat (without NCZ) was purchased and verified thorugh HPLC, that the chicken meat is NCZ-free (Table 1). Then, a known amount of NCZ was injected into the muscles of the meat and chopped into small pieces, then soaked in phosphate buffer (pH 5.0) and stirred for 30 min. Then, the solution is taken as a real sample, and the amperometric method was executed (Figure 6A). The electrode distributed fast gestures as laboratory samples.

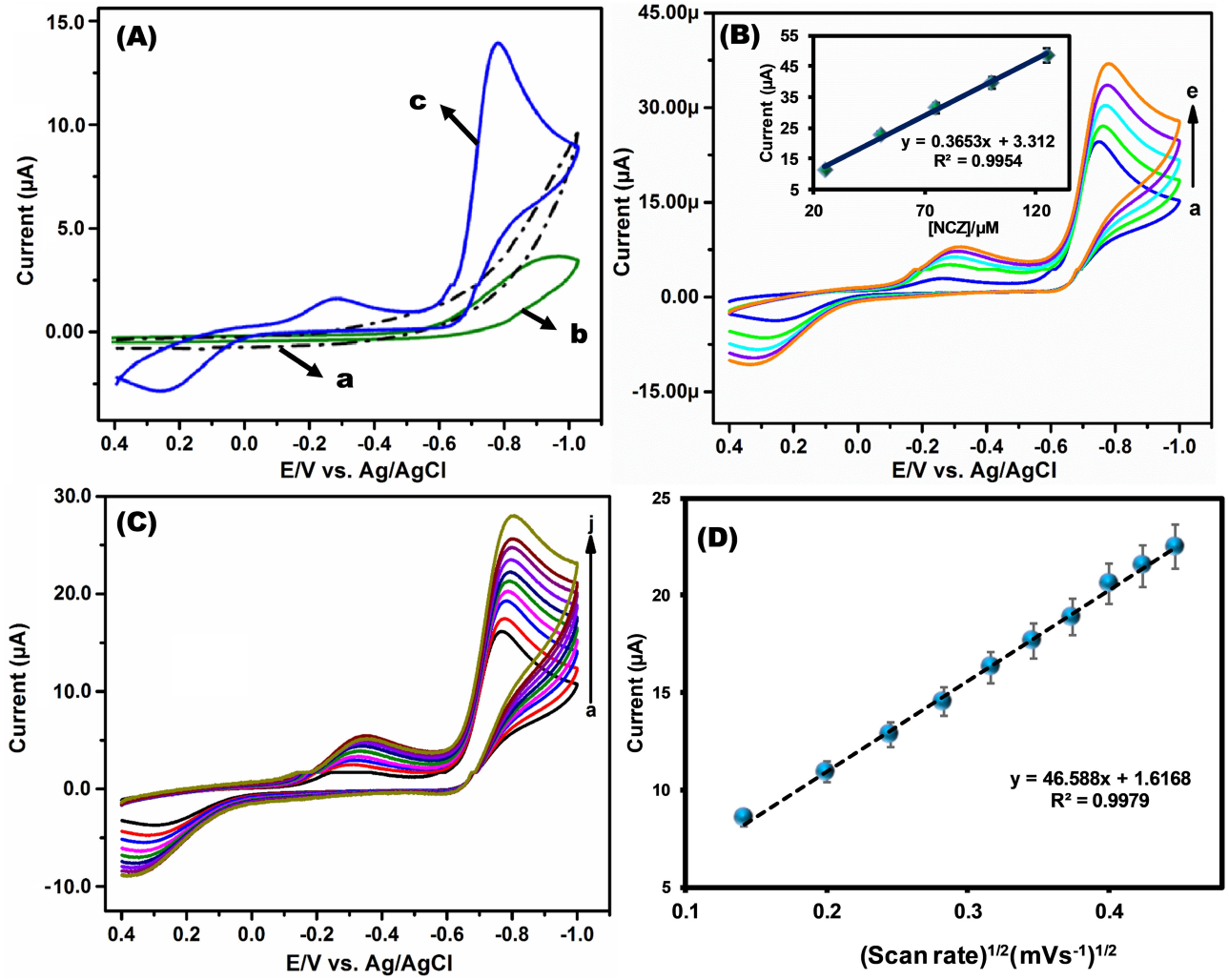


Fig. 3. (A) CVs obtained for unmodified SPCE electrode (a), PB/SPCE (c) in 0.1 M Phosphate buffer solution (pH 5) containing 25 μM NCZ, scan rate = 50 mV s^{-1} and blank of the PB/SPCE (b). (B) CVs of PB/SPCE in 0.1 M Phosphate buffer solution (pH 5) containing NCZ (a to e; 25 to 125 μM), scan rate = 50 mV s^{-1}. [Inset: [NCZ]/μM vs. current/μA] (C) CVs obtained at PB/SPCE in 0.1 M Phosphate buffer solution (pH 5) containing 25 μM NCZ at different scan rates (a to j; 20 to 200 mV s^{-1}). (D) (scan rate)$^{1/2}$/(mV s^{-1})$^{1/2}$ vs. peak currents (μA).

Table 1. Determination of NCZ in real samples using PB/SPCE and compared with HPLC method.

Sample	Spiked (μM)	Found (μM) AMP-*it*	HPLC	Relative error (%)	RSD (%)	Average Recovery (%)
Chicken	Fresh sample	0	0	–	–	
	5.0	4.82	4.91	1.86	3.78	
	10	9.76	9.87	1.12	2.97	99.02
	20	19.74	19.92	1.01	2.56	
Egg	Fresh sample	0	0	–	–	
	5.0	4.76	4.89	2.62	3.26	
	10	9.63	9.82	1.89	2.45	97.84
	20	19.34	19.87	2.3	3.32	

* Related standard deviation (RSD) of 3 independent experiments

The results obtained through the amperometric method are compared to HPLC method in (Table 1). Finally, it owned the wider linear range for the chicken meat sample between 5.2×10^{-6} and 1.35×10^{-3} mol L^{-1}, and it reached the LOD of 8.05×10^{-8} mol L^{-1} with the sensitivity of 775.2 μA/mM/cm^2 (Figure 6B). Food industrialists want indicative devices to confirm and quantifies the existence of NCZ added for prophylaxis. Likewise, this method

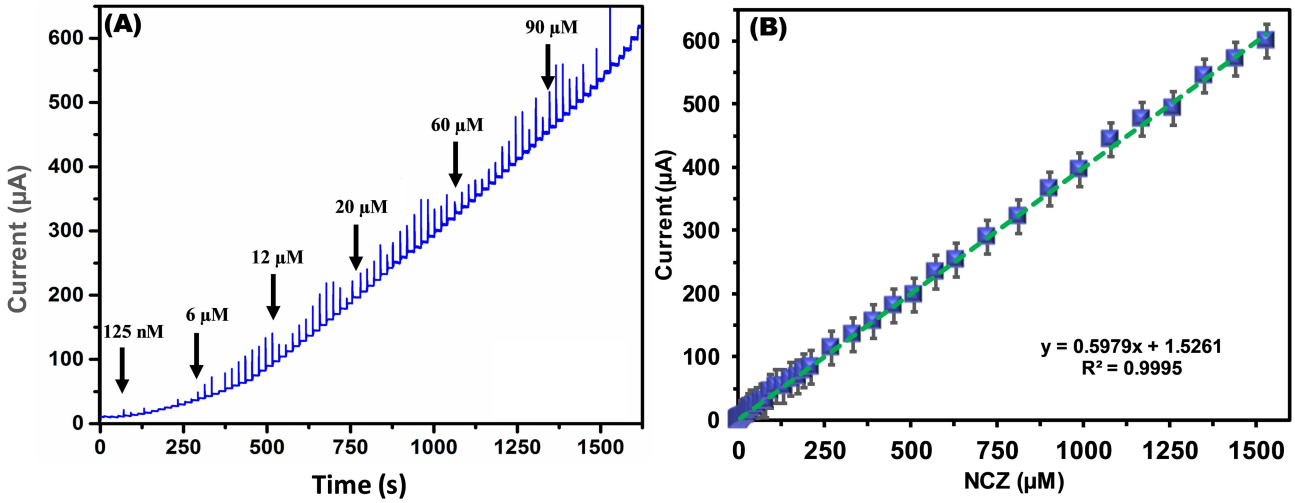


Fig. 4. (A) Amperometric responses of PB cubes film modified RDE for every sequential addition of NCZ into 0.1 M PB (pH 5). The rotating speed = 1200 RPM. (B) Calibration plot between [NCZ]/μM, and current (μA); working potential (E_{app}) = −0.79 V (vs. Ag/AgCl).

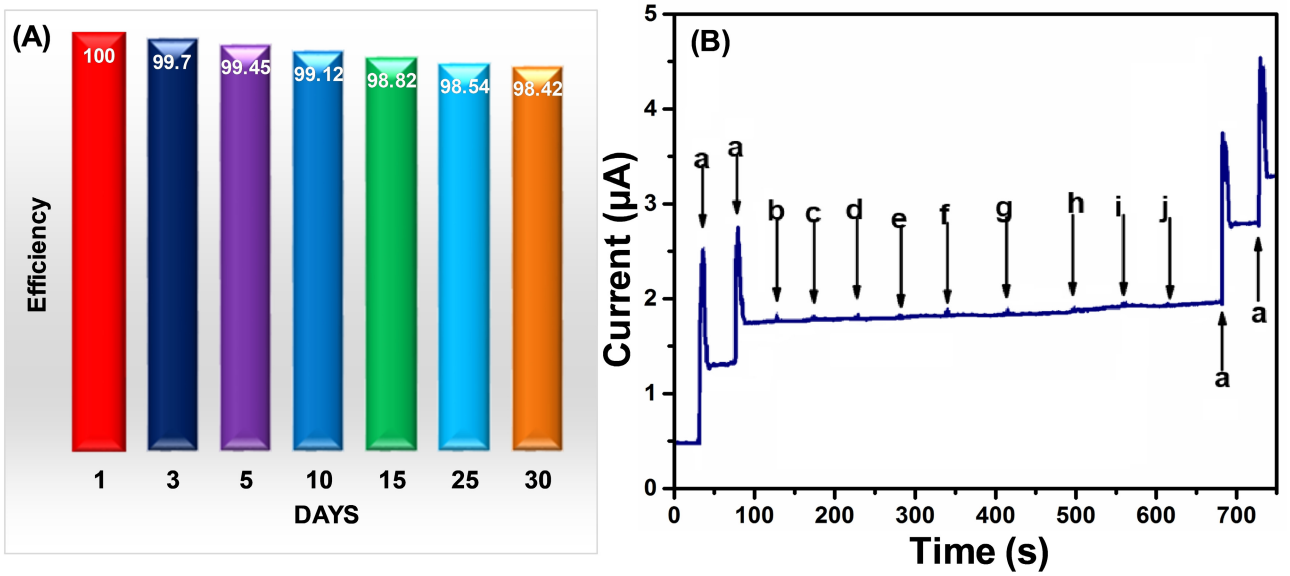


Fig. 5. (A) Stability plot of the sensor as its sequential usage for one month. (B) Amperometric response of film modified electrode toward 5 μM of nicarbazin (a), and 50 μM of sulfadiazine (b), amprolium (c), diclazuril (d), sulfacetamide (e), sulfaguanidine (f), D-penicillamine (g), doxycycline (h), clazuril (i), ponazuril (j) into 0.1 M PB (pH 5.0), Electrode rotation speed = 1200 RPM and applied potential = −0.79 V.

disclosed virtuous practical applicability in spiked egg samples. Before the NCZ spiking, the egg sample was tested and confirmed, that it is NCZ-free (Figure S3). For the sample preparation, the fresh egg was spiked with the quantified amount of NCZ and stirred well. The NCZ spiked egg was diluted with (pH 5) buffer solution under magnetic stirring (30 min) and taken for amperometric analysis. As a final point, it possessed the wide-ranging linearity for the egg sample between 5×10^{-6} and 1.59×10^{-3} mol L^{-1} and the attained LOD was 8.03×10^{-8} mol L^{-1} with the satisfactory sensitivity of 985.5 μA/mM/cm^2 (Figure 6C, D). The analytical parameters obtained at PB/SPCE towards NCZ in chicken and egg samples are compared with established analytical methods (Table S1). Satisfying the requirements for the cheap and responsive electrochemical device, here an advantageous, as well as an instantaneous analytical tool for the detection of NCZ in chicken meat and egg samples, is developed.

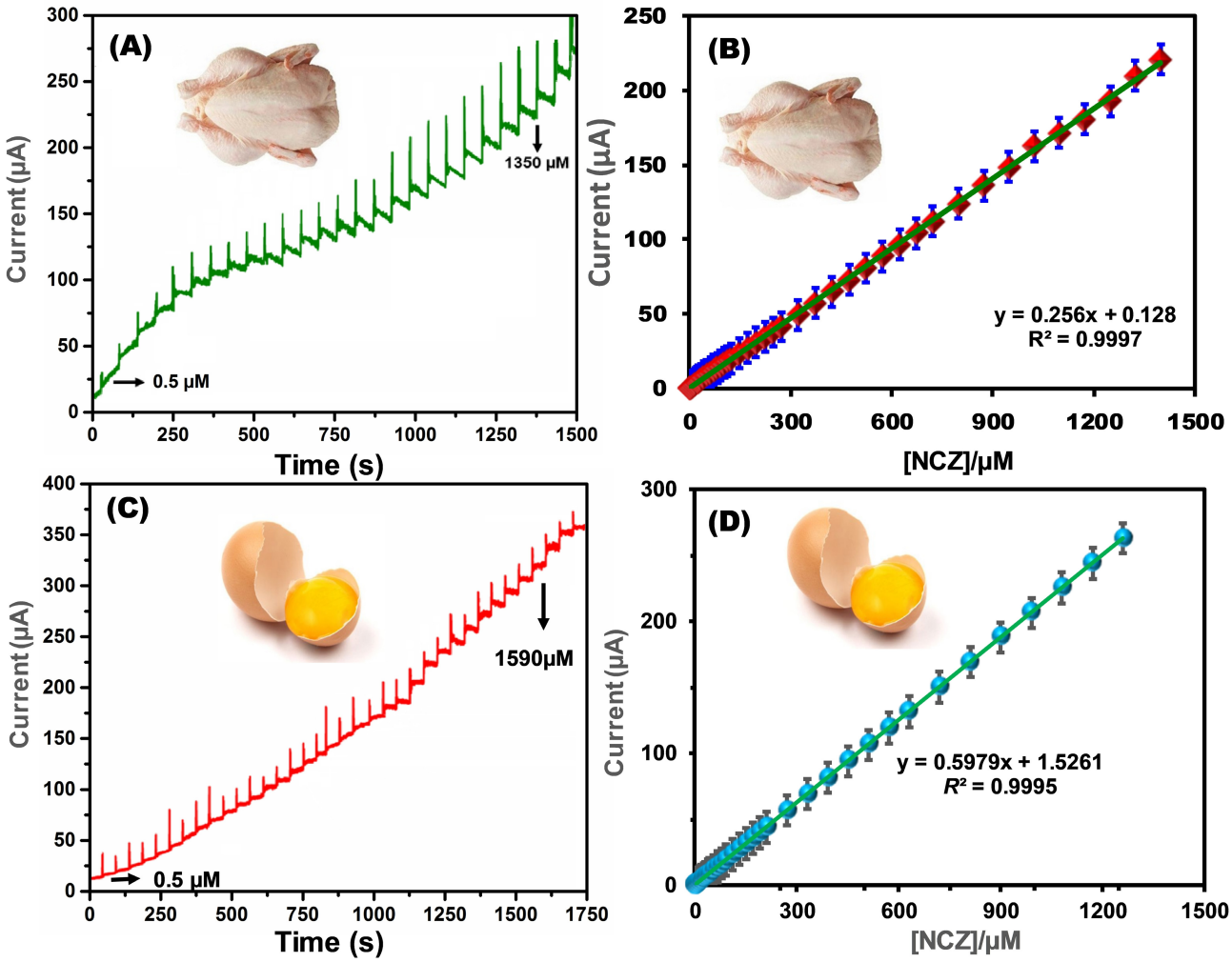


Fig. 6. Amperometric response for each sequential addition of real samples containing spiked NCZ into 0.1 M PB (pH 5.0). (A) Chicken meat sample, and (C) Egg sample. Calibration plots for chicken meat (B), and egg samples (D), $E_{app} = -0.79$ V (vs. Ag/AgCl).

4 Conclusions

The PB cubes validated an incredibly responsive, reproducible and hard-wearing NCZ electrochemical detector. The material was synthesized via simplistic green approach, and its practical materialization was publicized by FE-SEM, XRD, EDX, EIS and electrochemical methods. The PB/SPCE exhibited exceptional electrocatalytic capability towards NCZ reduction. Mostly, the detection of prophylactic antibiotic drug NCZ through the electrochemical process is novel to the field of electrochemistry as well as sensors. The assay procedure was also simple, responsive, and reproducible. This technique tends to be creative in the detection of NCZ contained in the samples of chicken meat and egg. The future work will be focused on the fabrication of PB cubes incorporated stretchable sensor devices for the real-time tracking and quantification of nicarbazin. Therefore, it holds greater perspective in food industries and poultry welfare.

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