

## **A novel and Disposable Amperometric Hydrazine Sensor based on Polydimethyldiallylamine Stabilized Copper(II)hexacyanoferrate Nanocubes modified Screen-printed Carbon Electrode**

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A cubic shaped copper(II)hexacyanoferrate was prepared by wet chemical method by mixing an equimolar concentration of  $\text{CuCl}_2$  with  $\text{K}_3[\text{Fe}(\text{CN})_6]_2$  in the presence of poly(diallyldimethylammonium chloride) (PDDA). The X-ray diffraction, field emission scanning electron microscopy, elemental analysis, Fourier transform infrared spectroscopy and thermal gravimetric analysis were used to confirm the formation of PDDA stabilized copper(II)hexacyanoferrate nanocubes (PDDA@copper(II)hexacyanoferrate nanocubes). The electrocatalytic behavior of the PDDA@copper(II)hexacyanoferrate nanocubes modified screen-printed carbon electrode (SPCE) towards electrochemical oxidation of hydrazine was studied by cyclic voltammetry (CV). The CV results revealed that PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE exhibits an enhanced electrocatalytic activity and lower oxidation potential towards hydrazine than bare SPCE. Under optimized conditions, amperometric *i-t* method was used for the determination hydrazine, and PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE can able to detect hydrazine in the linear concentration ranges from 0.03 to 533.6  $\mu\text{M}$  with a detection limit of 10 nM. The PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE is highly selective in the presence of potentially active interfering compounds including high concentration of ascorbic acid. In addition, the developed hydrazine sensor shows acceptable practicality with excellent long-term stability towards the detection of hydrazine.

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**Keywords:** Screen-printed carbon electrode; PDDA@copper(II)hexacyanoferrate nanocubes, PDDA, electro-oxidation, hydrazine, amperometry.

## 1. INTRODUCTION

Metal hexacyanoferrates are considered as one of the polynuclear mixed-valence materials, has recently attracted widespread attention due to their useful electron transfer mediator for various kind oxidation and reduction reactions [1]. Potential applications of these systems are in such areas as sensors, charge capacitors, display devices and molecular electronics, ion-exchange selectivity, electrochromism, solid-state batteries and magnetisms [1-4]. Among the transition metal hexacyanoferrates, copper(II)hexacyanoferrate are considered as model system because of their reversible electrochemical behaviors in aqueous supporting electrolytes containing not only  $K^+$  but also other alkali metal cations such as  $Li^+$ ,  $Na^+$ ,  $Rb^+$  or  $Cs^+$  [5, 6]. Apparently, both oxidized and reduced structures of copper(II)hexacyanoferrate are open enough to permit a flux of alkali metal cation of different sizes. The zeolitic structure of Prussian blue and its analogues, generally metal hexacyanoferrates permits the flux of different ions into the channels of the three-dimensional network, allowing some reversible redox reactions [7]. For instance, Malinauskas described the electrocatalytic reduction of hydrogen peroxide as well as the operational stability of copper(II)hexacyanoferrate modified carbon paste electrodes [7, 8]. Brett research group demonstrated the use of copper(II)hexacyanoferrate modified electrodes in sensors as well as biosensor applications [9]. Baioni and co-authors have studied the electrocatalytic properties of copper(II)hexacyanoferrate nanoparticles for the determination of hydrogen peroxide by using the electrostatic layer-by-layer (LBL) deposition of the electrocatalyst to modify fluorine doped tin oxide electrode [10, 11].

Hydrazine is widely used in several fields such as agricultural chemicals (pesticides), blowing agents, pharmaceutical intermediates, photographic developers, treatment of water for corrosion protection, textiles dyes, jets and rocket fuels, missile system, catalyst, emulsifier, corrosion inhibitor and reducing agents [12-14]. Individuals may be occupationally exposed to hydrazine in the workplace or accidental discharges into water, air and soil, which may occur during storage, handling, transport, and improper waste disposal. Several different methods have been reported in the literature like spectrophotometric [15], optical [16], potentiometric [17], spectrophotometric flow injection [18], fluorimetric [19, 20], and chemiluminescence [21, 22] were used to detect hydrazine. Among the other techniques, electrochemical method is considered as a simple and cost-effective method for the determination of hydrazine at low concentration ranges. Amperometric detection of hydrazine which could be include electrodes like chemically modified electrode containing specifically select redox mediator immobilized on conventional electrodes such as platinum, gold, rhodium, palladium as being electrocatalytic for the oxidation of hydrazine [23-26].

Unfortunately, hydrazine needs a high overpotential for oxidation with conventional electrodes but modified electrodes that lower the over potential can be a good alternative for this purpose. Moreover, various chemically modified electrodes have been applied in the determination of hydrazine. For instance, cobalt phthalocyanine [27], ruthenium cyanide [28], cobalt

tetraphenylporphyrin [29], inorganic mixed valent Prussian blue [30], oxymanganese [31], vitamin B<sub>12</sub> [32], platinum particles [33], chlorogenic acid [34], cobalt pentacyanonitrosylferrate [35], cobalt hexacyanoferrate [36] and nickel hexacyanoferrate [37] have been used as modifiers in the conventional carbon electrodes. Only limited reports have been appeared in the literature on electrocatalytic activity of metal hexacyanoferrate nanoforms [38, 39]. Mostly, metal hexacyanoferrate thin film modified carbon nanotube and graphene supports have been utilized for the electrochemical detection of hydrogen peroxide and biomolecules [40]. Herein, we demonstrate that the electrochemical detection of hydrazine using PDDA supported cubic shaped copper(II)hexacyanoferrate modified screen-printed carbon electrode (SPCE) for the first time. The positively charged polymer electrolyte first interact with the negatively charged ferricyanide ion and then form a stable copper(II)hexacyanoferrate nanocubes in presence of Cu<sup>2+</sup> in the reaction medium.

## 2. EXPERIMENTAL

### 2.1. Materials and method

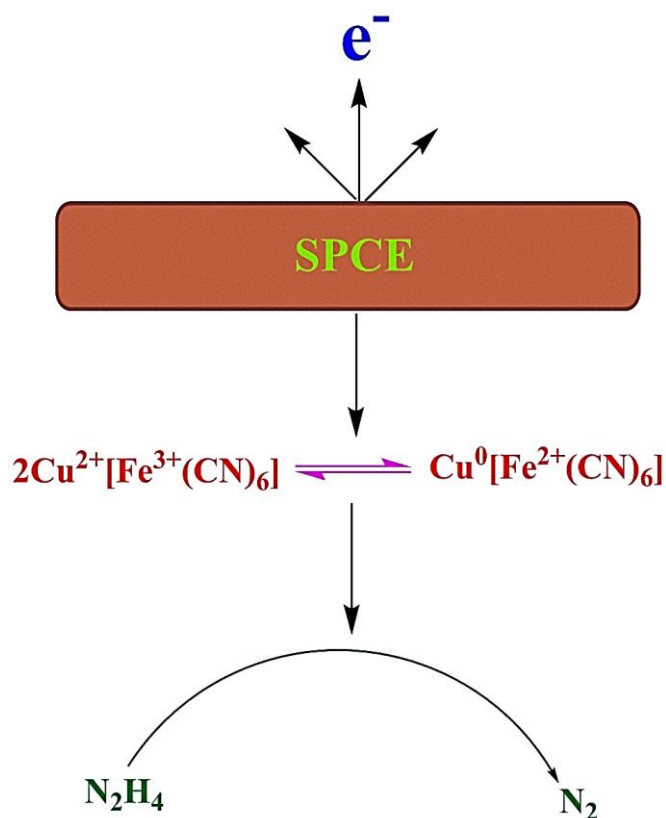
Screen-printed carbon electrode with an active surface area about 0.08 cm<sup>2</sup> was purchased from Zensor R&D Co., Ltd., Taipei, Taiwan. Copper chloride (CuCl<sub>2</sub>), potassium hexacyanoferrate K<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub> and 2% poly(diallyldimethylammonium chloride) were purchased from Sigma Aldrich, Bangalore, India. Isopropanol and acetone were received from SRL Pvt. Ltd., India. The supporting electrolyte pH 7.0 was prepared using 0.05 M Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> and pH were adjusted with either 0.5 M H<sub>2</sub>SO<sub>4</sub> or 2 M NaOH. The stock solutions were prepared using Millipore water.

Powder X-ray diffraction analysis (XRD) was taken using JSO DEBYE FLEX 2002 Seifert diffractometer. Field emission scanning electron microscopic (FESEM) image of PDDA@copper(II)hexacyanoferrate was acquired using JEOL-JSM-6360 field emission scanning electron microscope. Fourier transform infrared spectroscopy (FTIR) was performed using Nicolet Nexus 670 spectrometer. Thermo gravimetric analysis (TGA) was performed Perkin-Elmer TG analyzer. Electrochemical measurements such as cyclic voltammetry and amperometric *i-t* were performed using CHI model 1205B electrochemical workstation from CH instruments. A standard three-electrode setup was used for electrochemical experiments, where modified SPCE as working electrode, saturated Ag/AgCl as a reference and a platinum wire as an auxiliary electrodes.

### 2.2. Synthesis of PDDA@copper(II)hexacyanoferrate nanocubes and electrode preparation

The PDDA@copper(II)hexacyanoferrate nanocubes was prepared by using PDDA as stabilizing agent. First, 0.01 M CuCl<sub>2</sub> was added into the 0.1 M K<sub>3</sub>Fe(CN)<sub>6</sub> in 1:1 molar ratio in presence of 2% PDDA. The solution was stirred constantly and the solution was turned to brown after 10 mins, which indicating the formation of PDDA@copper(II)hexacyanoferrate. It is well known that the metal hexacyanoferrate nanocubes formed instantaneously due to the rapid reaction between metal salts and ferricyanide ions. The PDDA@copper(II)hexacyanoferrate was isolated by precipitation by the addition of isopropanol followed by the addition of acetone. The as-prepared

PDDA@copper(II)hexacyanoferrate nanocubes was centrifuged and washed with acetone. The resulting product was dried in an inert atmosphere under vacuum at room temperature for 12 h. The PDDA@copper(II)hexacyanoferrate nanocubes was re-dispersed (1 mg/mL) in ethanol for further use. For electrode modification, about 8  $\mu\text{L}$  of as-prepared PDDA@copper(II)hexacyanoferrate nanocubes dispersion was dropped on SPCE and dried in an air oven. The resulting PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE was used for further electrochemical studies. The overall procedure on formation of PDDA@copper(II)hexacyanoferrate nanocubes is illustrated in Scheme 1.



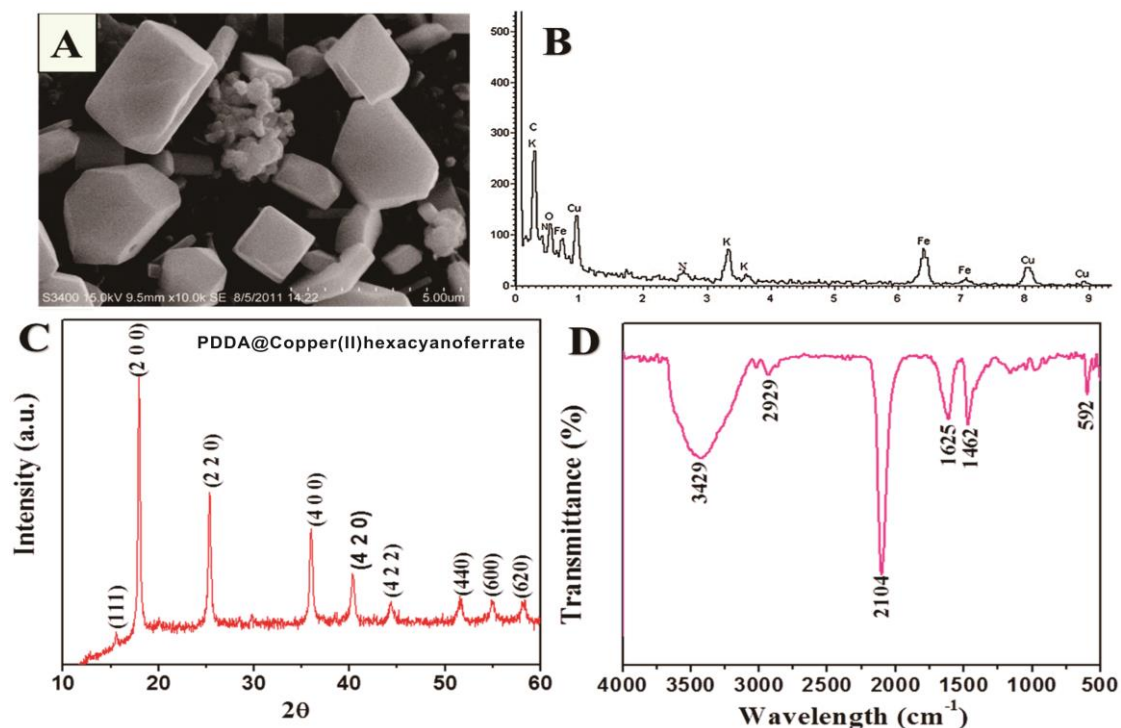
**Scheme 1.** Schematic representation of the formation of PDDA@copper(II)hexacyanoferrate and its electrocatalytic oxidation towards hydrazine.

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization of PDDA@copper(II)hexacyanoferrate nanocubes

Fig. 1A shows the high quality FESEM image of as-synthesized PDDA@copper(II)hexacyanoferrate nanocubes and observed that the copper(II)hexacyanoferrate have regular cubic shaped particles with various sizes. In addition, PDDA@copper(II)hexacyanoferrate exhibited uniformly distributed cubes with an average particle size of  $210 \pm 40$  nm. The elemental composition of PDDA@copper(II)hexacyanoferrate nanocubes is analyzed by elemental analysis

(EDS) and corresponding EDS is shown in Fig. 1B. It can be seen that the elemental ratio of Cu/Fe is closer to one and a smaller amount of K is observed from the EDS. The result indicates that the potassium ions freely occupied in the FCC lattice and confirmed the formation of copper(II)hexacyanoferrate Fig. 1C shows the XRD pattern of PDDA@copper(II)hexacyanoferrate nanocubes.

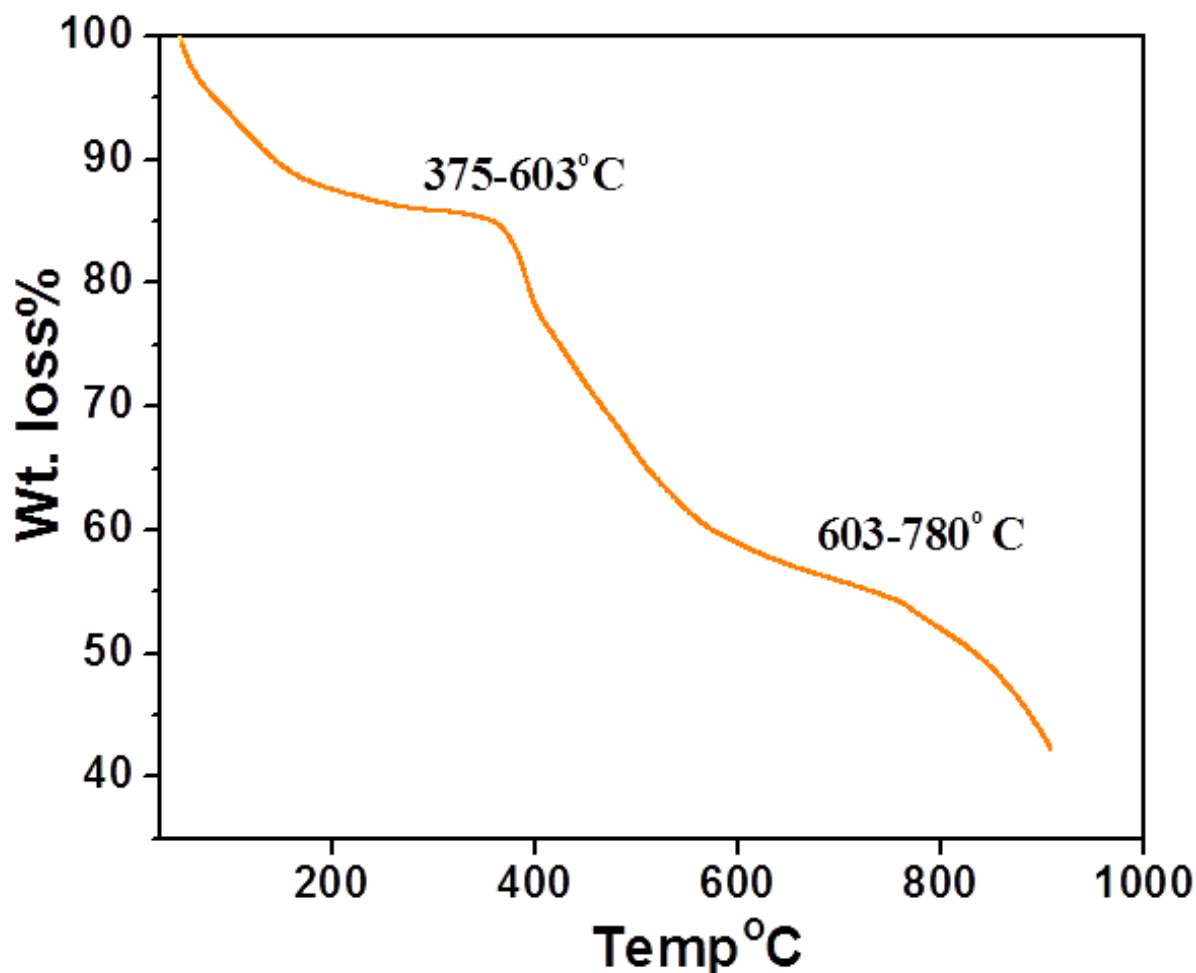


**Figure 1.** A) High-resolution FESEM image of PDDA@copper(II)hexacyanoferrate nanocubes. B) EDX analysis of PDDA@copper(II)hexacyanoferrate. C) XRD pattern and FTIR spectrum (D) of PDDA@copper(II)hexacyanoferrate nanocubes.

The XRD pattern of PDDA@copper(II)hexacyanoferrate shows several broad diffraction peaks. The peak positions at  $2\theta$  value of  $17.35^\circ$ ,  $24.58^\circ$ ,  $35.16^\circ$  and  $39.45^\circ$  are assigned to the (200), (220), (400), and (420) planes of the face centered cubic (FCC) structure of copper(II)hexacyanoferrate nanocubes [41]. The crystallite size of copper(II)hexacyanoferrate nanocubes was calculated from (200) plane using the Debye–Scherrer. The average crystallite size was 230 nm, which is more consistent with the crystallite size of copper(II)hexacyanoferrate nanocubes in FESEM. Fig. 1D shows the FTIR spectrum of PDDA@copper(II)hexacyanoferrate. The FTIR spectrum of PDDA@copper(II)hexacyanoferrate shows a broad peak around  $3429\text{ cm}^{-1}$  due to the -OH stretching of  $\text{H}_2\text{O}$  molecules [42]. The sharp peak was observed at 2929, 2104 and  $592\text{ cm}^{-1}$ , which are due to the -CN stretching of -CN-Fe-CN-,  $\text{Fe}^{2+}$ -CN-  $\text{Fe}^{2+}$ -and Fe-CN- from PDDA@copper(II)hexacyanoferrate. In addition, another sharp peak around  $625\text{ cm}^{-1}$  and  $1462\text{ cm}^{-1}$  is observed, which are due to the bending vibrations of the interstitial water and that of coordinated water respectively. From the above

studies, it is concluded that copper(II)hexacyanoferrate were effectively protected with the positively charged PDDA polymer.

Fig. 2 shows the TGA of PDDA stabilized copper(II)hexacyanoferrate nanocubes. The decomposition of polymer stabilized copper(II)hexacyanoferrate nanoparticles are occurring near to decomposition of copper(II)hexacyanoferrate. A similar thermal decomposition behavior of metal hexacyanoferrate has been reported recently with a similar decomposition pattern [43].

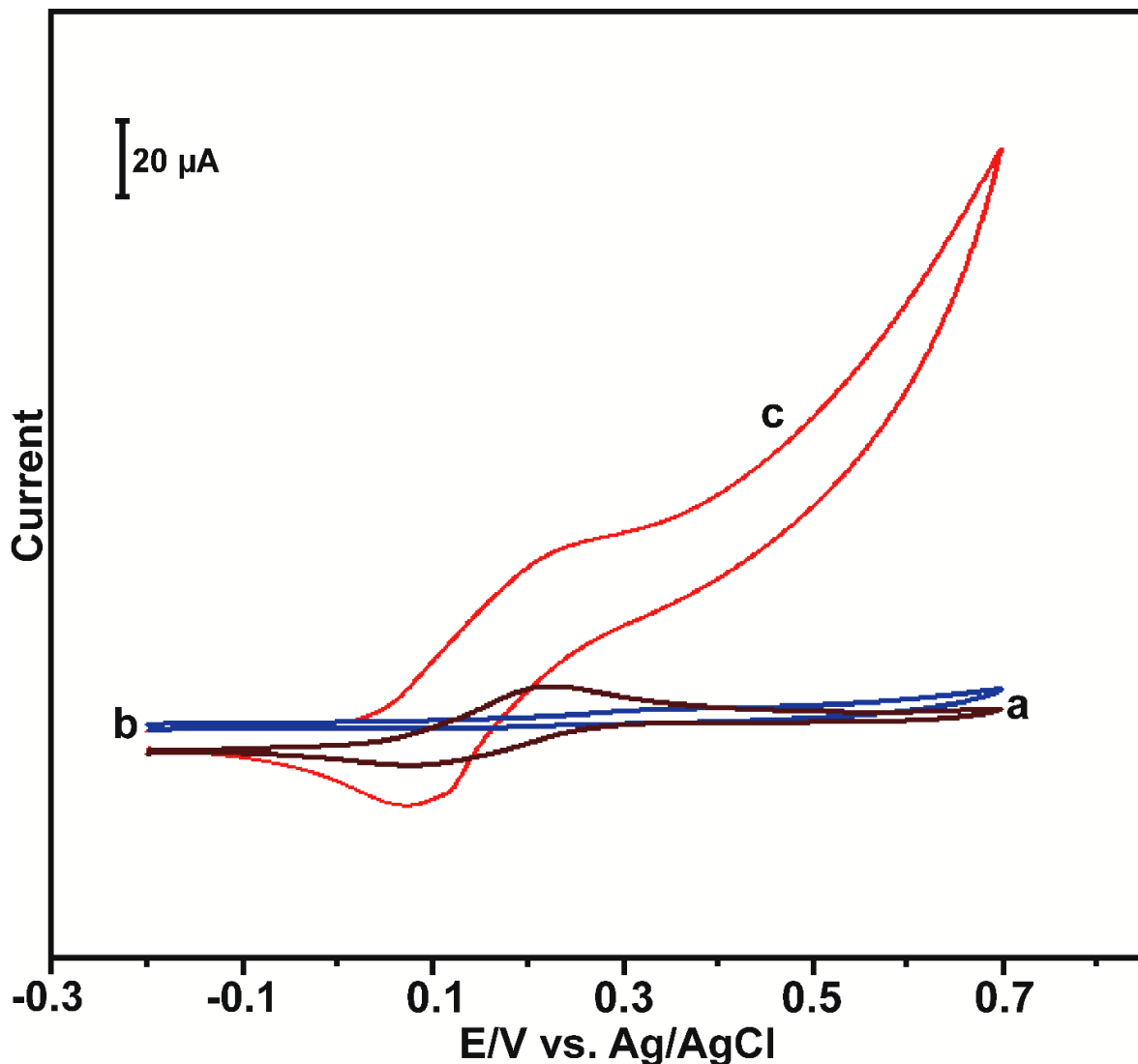


**Figure 2.** TGA analysis of PDDA@Copper(II)hexacyanoferrate nanocubes.

The first stage is from 30 to 148 °C, over which a mass loss of about 33% was observed due to dehydration. If the heating temperature is higher than 400°C, the above copper(II)hexacyanoferrate form alloy nanoparticles. It is inferred that copper(II)hexacyanoferrate undergoes thermal decomposition, which leads to the formation of Cu-Fe alloy as shown in the previous experimental studies.

### 3.2. Electrocatalytic oxidation of hydrazine

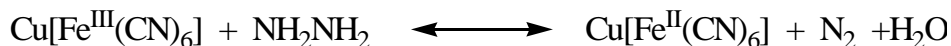
The electrochemical oxidation of hydrazine using different modified SPCEs in 0.1 M phosphate buffer pH 7.0 was investigated by CV. Fig. 3 shows the cyclic voltammograms of bare (a) and PDDA@copper(II)hexacyanoferrate nanocubes (c) modified electrodes in 1 mM hydrazine containing pH 7.0 at a scan rate of 50 mV/s.



**Figure 3.** Cyclic voltammograms obtained for bare (a) and PDDA@copper(II)hexacyanoferrate nanocubes (c) modified electrodes in 1 mM hydrazine containing pH 7.0 at a scan rate of 50 mV/s. At same conditions, PDDA@copper(II)hexacyanoferrate nanocubes modified electrode in the absence (b) of hydrazine.

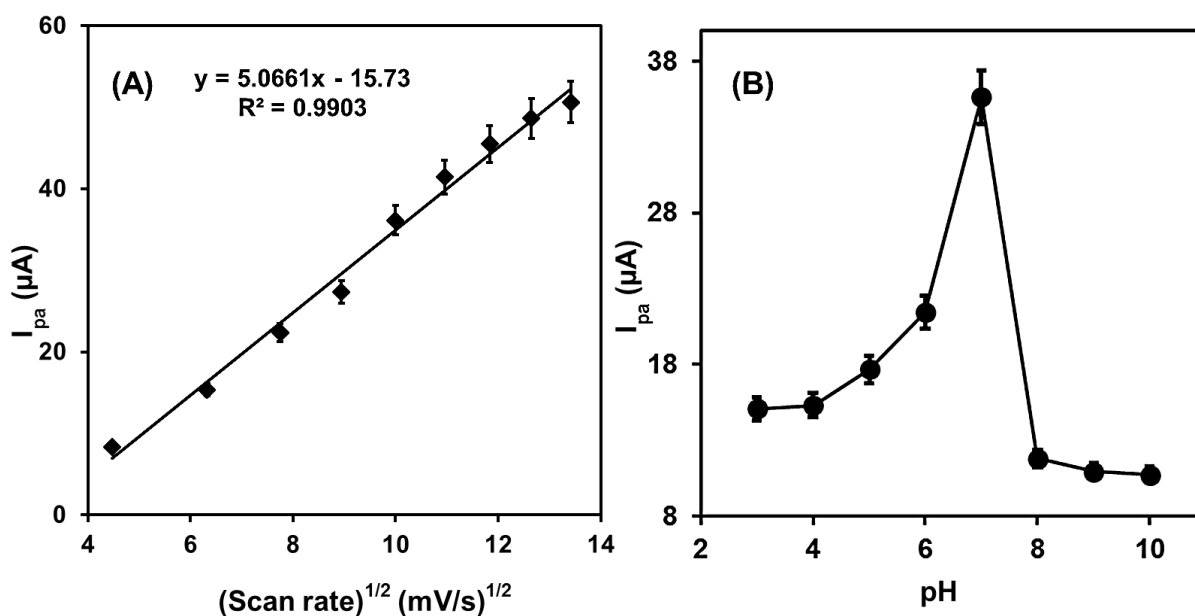
It can be seen that the bare SPCE did not show obvious response for the presence of 1 mM hydrazine, which indicates the poor electrocatalytic ability of bare SPCE. On the other hand, PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE shows an enhanced oxidation peak at 0.2 V for the presence of hydrazine. The result indicates that the PDDA@copper(II)hexacyanoferrate

nanocubes promotes a higher electrocatalysis rate for hydrazine oxidation at the modified electrode surface. During the cyclic voltammograms, there is no enhanced oxidation peak was observed for absence of hydrazine (b), however a clear redox couple was observed for  $\text{Fe}^{\text{II/III}}$  redox couple. The result clearly indicates that the enhanced oxidation peak current response of  $\text{Fe}^{\text{II/III}}$  redox couple is due to the presence of hydrazine. The typical electrocatalytic oxidation of hydrazine using the PDDA@copper(II)hexacyanoferrate nanocubes modified electrode system is shown in the following equation:



### 3.3. Effect of scan rate and pH

The effect of the scan rate was investigated using PDDA@copper(II)hexacyanoferrate nanocubes modified electrode in 1 mM hydrazine containing pH 7.0 at a scan rate of 50 mV/s by cyclic voltammetry. The obtained anodic peak current response vs. square root of scan rates is plotted in Fig. 4A. It can be clearly seen that the anodic peak current response of hydrazine was linear against the square root of scan rates from 20 to 200 mV/s with the correlation coefficient of 0.9903. The result indicates that the electro-oxidation of hydrazine at PDDA@copper(II)hexacyanoferrate nanocubes modified electrode is controlled by a diffusion process rather than absorption process [44, 45].



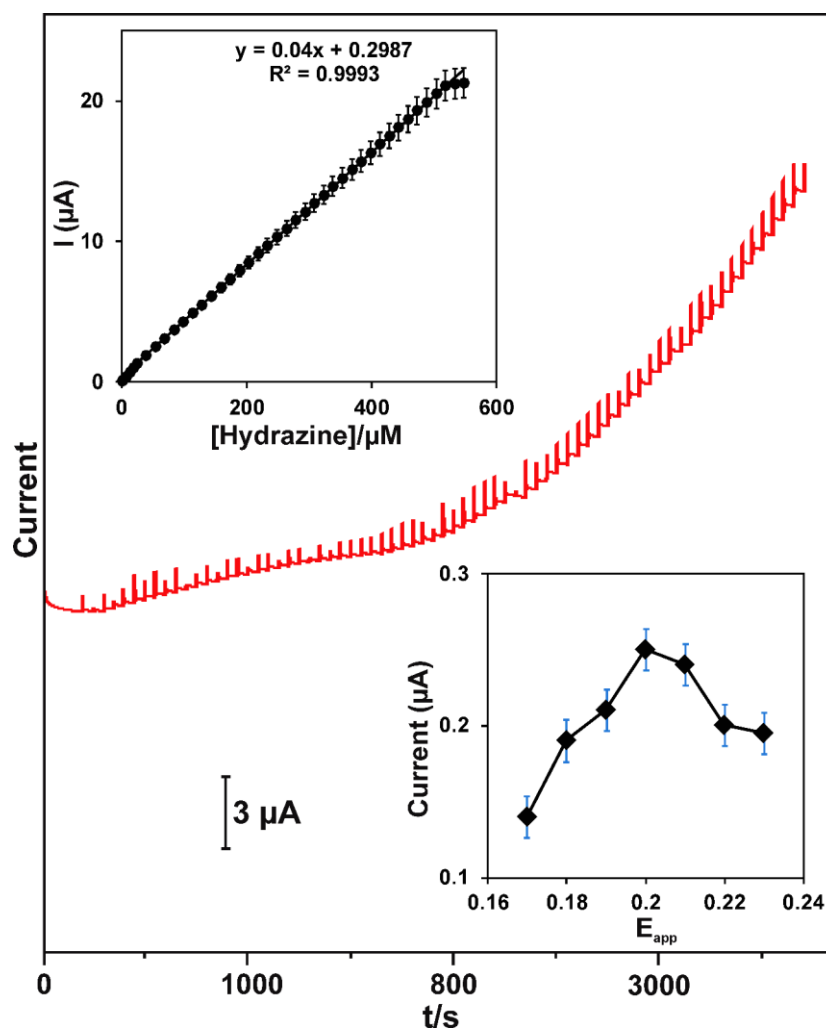
**Figure 4.** A) Plot of anodic peak current response of 1 mM hydrazine vs.  $(\text{scan rate})^{1/2}$ . B) Plot of anodic peak current response of 1 mM hydrazine vs. pH. The experimental conditions are similar to Fig. 3.

We have also investigated the effect of pH on the oxidation peak current response of hydrazine and obtained results are plotted in Fig. 4B. A maximum oxidation peak current response of hydrazine was found at pH 7.0 and was decreased above or below pH 7.0. Hence, pH 7.0 is used as an optimum pH for further electrochemical studies.



### 3.4. Amperometric determination of hydrazine

A typical hydrodynamic amperometry was used for the determination of hydrazine using PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE. Before amperometric measurements, effect of different applied potential on the amperometric current response of PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE towards 1  $\mu\text{M}$  hydrazine was studied. Amperometry measurements were performed in constantly stirred pH 7.0 at different applied potentials and the corresponding results were plotted in Fig. 5 lower inset. It can be seen that a maximum sensitivity of hydrazine was obtained for 0.2 V applied potential and it can be used for amperometric measurements.



**Figure 5.** Amperometric response of PDDA@copper(II)hexacyanoferrate nanocubes modified electrode for the successive additions of different concentration of hydrazine (0.03–548.6  $\mu\text{M}$ ) in constantly stirred pH 7.0 at an applied potential of 0.2 V. Inset (upper) shows the linear relationship of amperometric current vs. [hydrazine]. Inset (lower) shows the effect of applied potential vs. current response.

Fig. 5 shows the typical current-time profile for successive addition of different concentration of hydrazine (0.03–548.6  $\mu\text{M}$ ) into the continuously stirred pH 7.0. A well-defined amperometric current response was observed for each addition of different concentration of hydrazine and reaching a

fast dynamic equilibrium at PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE. The response time of the sensor was 2 s, which indicates the fast diffusion of hydrazine on PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE. The obtained amperometric current response was plotted against concentration of hydrazine and the linear calibration plot is shown in Fig. 5 upper inset. Furthermore, PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE is linear over the hydrazine concentration ranging from 0.03 to 533.6  $\mu\text{M}$  with the correlation coefficient of 0.9993. The detection limit (LOD) was found to be 10 nM based on  $3 \times \text{Sd}$  of the blank response/slope of the calibration plot. In addition, the sensor also shows a good sensitivity for the determination of hydrazine. To illustrate the advantage of sensor, the LOD and linear response range was compared with previously reported hydrazine sensors and comparative results are in Table 1.

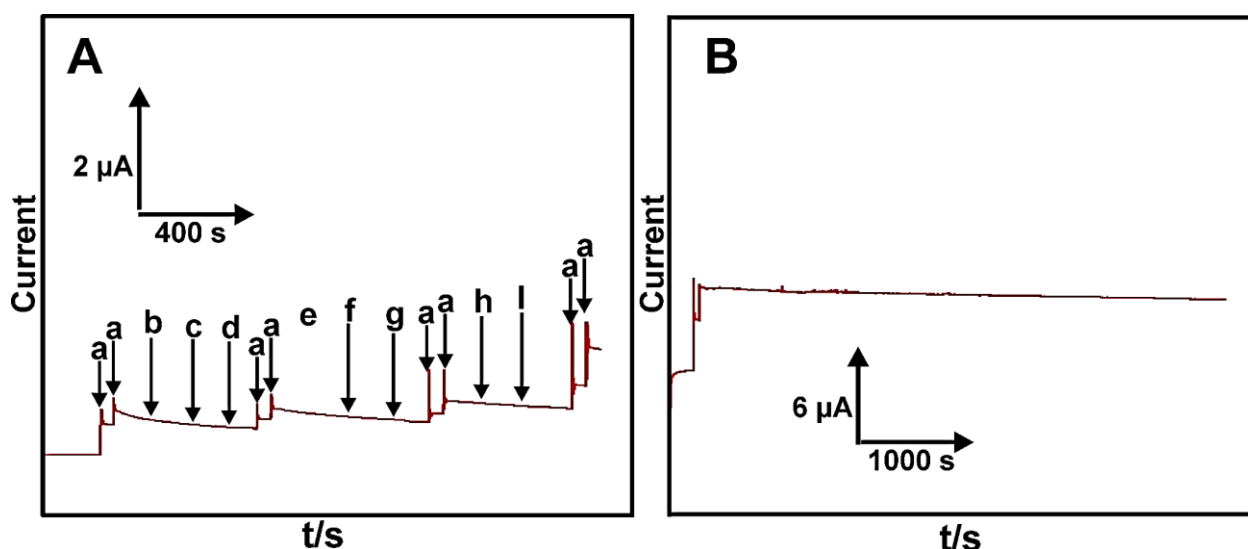
**Table 1.** Comparison of analytical features (LOD and linear response range) of PDDA@copper(II)hexacyanoferrate nanocubes modified electrode for hydrazine with previously reported modified electrodes for the determination of hydrazine.

Modified electrode	pH	Linear response range	LOD ( $\mu\text{M}$ )	Ref.
NiHCF@TiO <sub>2</sub> /GCE	8.0	$0.2 \times 10^{-6} - 1 \times 10^{-6}$	0.1	[46]
NBHCF-CPE/GCE	7.0	$0.1 \times 10^{-3} - 6 \times 10^{-3}$	40.0	[47]
CoHCF@TNT/GCE	7.0	$5 \times 10^{-4} - 2.5 \times 10^{-3}$	1000.0	[48]
NiHCF/GCE	7.0	$2 \times 10^{-5} - 2 \times 10^{-3}$	8.0	[35]
BiHCF/CCE	7.0	$7 \times 10^{-6} - 1.1 \times 10^{-3}$	3.0	[49]
NiHCF/GCE	7.0	$2.4 \times 10^{-6} - 8.25 \times 10^{-3}$	1.0	[50]
CeHCF/OMC/GCE	7.0	$1 \times 10^{-3} - 1.63 \times 10^{-4}$	0.1	[51]
ZrHCF/Au-PtNPs/NFs/CNT/GCE	7.0	$0.15 \times 10^{-6} - 1.1 \times 10^{-4}$	0.09	[52]
NiHCF/CCE	7.0	$2 \times 10^{-3} - 50 \times 10^{-3}$	0.28	[53]
MnHCF/GCE	7.0	$3.3 \times 10^{-5} - 8.18 \times 10^{-3}$	6.65	[54]
PDDA@ copper(II)hexacyanoferrate /SPCE	6.5	$0.03 \times 10^{-6} - 536.6 \times 10^{-6}$	0.01	Present work

The comparison table clearly reveals that PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE has lower LOD with wider linear range over previously reported modified electrodes for the determination of hydrazine [46–54]. Hence, PDDA@copper(II)hexacyanoferrate nanocubes can be used as promising electrode material for the sensitive and low-level determination of hydrazine.

### 3.5. Specificity of the sensor

It is well known that some compounds can be electroactive with hydrazine in the modified electrode and therefore the selectivity of the sensor was evaluated by amperometry. Under optimum conditions, the selectivity of PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE in the presence of potentially active compounds such as dopamine, uric acid, ascorbic acid, glucose,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ni}^{2+}$  was investigated and corresponding amperometric results are shown in Fig. 6A. It can be seen that the 100-fold addition ( $100\ \mu\text{M}$ ) of aforementioned interfering compounds had no effect on the PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE. On the other hand,  $1\ \mu\text{M}$  addition of hydrazine show a well-defined amperometric response on PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE. The result indicates that the high specificity of PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE towards the detection of hydrazine.



**Figure 6.** Amperometric *i-t* response of PDDA@copper(II)hexacyanoferrate nanocubes modified electrode for the addition of  $1\ \mu\text{M}$  hydrazine (a) and 100-fold addition of DA (b), UA (c), AA (d), glucose (e),  $\text{Cl}^-$  (f),  $\text{Na}^+$  (g),  $\text{Mg}^{2+}$  (h) and  $\text{Ni}^{2+}$  (i) into the constantly stirred pH 7.0. Working potential = 0.2 V. B) Long-term stability of PDDA@copper(II)hexacyanoferrate nanocubes modified electrode (up to 5000 s) after the addition of  $50\ \mu\text{M}$  hydrazine.

### 3.6. Long term stability and practicality of the sensor

The long-term stability of the PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE was examined up to 5000 s by amperometric method (Fig. 6B). Only 4.9% of the initial current response of  $50\ \mu\text{M}$  hydrazine was lost after the 5000 s continuously run in pH 7.0. The result indicates excellent long-term stability of the PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE. In order to validate its practical application, hydrazine was determined in tap and lake water samples by amperometry using standard addition method. The water sample was spiked with standard hydrazine solution with concentration of  $5.0\ \mu\text{M}$ . The obtained recoveries of hydrazine is tabulated in Table 2.

**Table 2.** Determination of hydrazine in water sample using PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE by amperometry (n = 3).

Sample	Detected ( $\mu\text{M}$ )	Added ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ )	Recovery ( $\mu\text{M}$ )	RSD (%)
Tap water	6.6	2.0	8.5	98.8	2.6
	6.6	5.0	11.5	99.1	2.9
Lake water	12.3	2.0	14.0	98.0	4.3
	12.3	5.0	16.7	96.0	4.1

It can be seen from Table 2 that the PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE has an appropriate practicality and the average recoveries were 99.0% and 98.0% for hydrazine in tap water and lake water samples, respectively. Therefore, as-prepared PDDA@copper(II)hexacyanoferrate nanocubes modified electrode can be used real time sensing of hydrazine in water samples.

#### 4. CONCLUSION

In summary, PDDA@copper(II)hexacyanoferrate nanocubes has been synthesized using a simple wet chemical method and used as an electrocatalyst for oxidation of hydrazine for the first time. The physicochemical characterizations confirmed the formation of PDDA@copper(II)hexacyanoferrate nanocubes. Compared with unmodified electrode, PDDA@copper(II)hexacyanoferrate nanocubes modified SPCE detects the hydrazine at lower potential with enhanced sensitivity. The PDDA@copper(II)hexacyanoferrate nanocubes modified electrode shows a lower LOD (10 nM) and wider linear response range (up to 533.6  $\mu\text{M}$ ) for the determination of hydrazine. In addition, the present method is simple, sensitive and can be used for real time sensing of hydrazine in real samples.

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