We report the preparation of star fruit-like thulium hexacyanoferrate (TmHCF) by using one-step electrochemical deposition in cyclic voltammetry technique. The electrochemically deposited star fruit-like TmHCF is exhibit unique electrocatalytic activity towards the detection of L-cysteine (L-Cys). The as-prepared TmHCF was characterized using different techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD), electrochemical impedance spectroscopy (EIS). The electrochemical activity of star fruit-like TmHCF was studied using cyclic voltammetry (CV), and differential pulse voltammetry (DPV). The modified electrode shows a considerable linear range, sensitivity and detection limit of about 0.5 to 8.92 µM, 48.479 µA µM$^{-1}$ cm$^{-2}$ and 16 nM respectively. Furthermore, the modified electrode was tested in the real samples analysis in urine and river water samples.

**Keywords:** Thulium hexacyanoferrate (TmHCF), electrochemical sensor, L-cysteine.

1. **INTRODUCTION**

L-cysteine (L-Cys) is the sulfur containing amino acid with formula C$_3$H$_7$NO$_2$S which plays an important role in living systems especially the biological activities of enzymes and proteins [1,2] and it act as an antioxidant which may prevent the liver diseases [3]. L-Cys found in many foods such as soybeans, beef, onions, sunflowers seeds, chicken, and oats. The referred amount of L-cys for daily intake of about 4.1mg. A person with 70kg weighting should consume around 287mg of L-Cys per day. It has found in many pharmaceutical applications; specifically, it is used in antibiotics, for the treatment of skin damage, and as a radioprotective agent. The shortage of the L-Cys causes much illness, such as slowed growth in children, de-pigmentation of hair, edema, lethargy, liver damage, and loss of muscle and sever skin problem [4, 5]. Hence, the probing of L-cys in body fluids, pharmaceuticals, and food samples is very significant [6]. Different techniques are using for the
determination of L-Cys such as flow injection method [7,8], capillary column liquid chromatography [9], pulse amperometric determination [10], electrochemiluminescence analysis [11] and electrochemical technique [12]. Among these all, the electrochemical techniques have considered as the promising technique owing to the relatively low cost, simplicity, low time consuming, high sensitivity, and selectivity [13].

Metal hexacyanoferrate is the type of stable coordination compounds with fcc lattice. Owing to the good stability, favorable capacitive behavior, photo reversible enhancement of magnetization, unique degradation efficiency, good selectivity and sensitivity, the metal hexacyanoferrate focused on different applications such as supercapacitor [14], battery [15], Electrocatalysis [16], photomagnetic and magneto optic devices [17], photocatalytic devices [18] and sensor [19]. In order to extend the application of metal hexacyanoferrate in the field of biosensor, the new types of rare metal hexacyanoferrate are developing with high stability of metal cyanide, cation exchange properties, efficient ionic conductivity and reversible redox properties [20, 21]. In 1994, karyakin et al., reported the first research article based on the application of metal hexacyanoferrate for glucose biosensor with high sensitivity and selectivity. In the past decades, many types of metal hexacyanoferrate have been prepared using different preparation methods such as reverse micelles [22,23], simple chemical co precipitation technique [24], biocatalyst reaction [25], and electrochemical deposition. Among these all preparation methods, electrochemical deposition is simple cost and low time consuming technique to prepare the metal hexacyanoferrate with different morphology such as microstar like dysprosium hexacyanoferrate [26], flower like samarium hexacyanoferrate [27], flower and christmas tree like cerium hexacyanoferrate [28], yttrium (III) hexacyanoferrate micro flowers [29], switching structures of praseodymium hexacyanoferrate [30].

In this work, we reported a star fruit like thulium hexacanoferrate (TmHCF) modified electrode by an electrochemical deposition technique using different electrolytes contain ferricyanide solution with Tm$^{3+}$. The electrochemically deposited micro flower TmHCF exhibits considerable sensitivity towards the sensing of L-cysteine. In addition, only a few reports are available for the synthesis, characterization and application of TmHCF for electrochemical sensor. Zuchao Meng et al., reported TmHCF based glucose electrochemical sensor. However, the further studies are carried out to prepare the TmHCF with different morphology with improved electrocatalytic activity.

2. EXPERIMENTAL SECTION

2.1. Materials

L-cysteine and Thulium (III) chloride hexahydrate were purchased from Sigma Aldrich. K$_3$Fe(CN)$_6$ was purchased from Wako pure chemical industries. Electrocatalytic studies were carried out in 0.5 M KCl solution. All the solutions were prepared using doubly distilled water. All chemicals are analytical grade and used as received without any further purification.
2.2. Apparatus

Scanning Electron Microscopy (SEM) was performed using Hitachi S-3000 H electron microscope. Energy dispersive X-ray (EDX) spectrum was recorded using HORIBA EMAX X-ACT that was attached with Hitachi S-3000 H scanning electron microscope. XRD characterization was carried out using XPERT-3 diffractometer with Cu Kα radiation (K= 1.54 Å). The Cyclic Voltammetry (CV) studies were performed by using CHI1205B electrochemical analyzer and Differential Pulse Voltammetry study were performed by using CHI900 electrochemical analyzer. Conventional three-electrode system was used for the electrochemical experiments, glassy carbon electrode (GCE) was used as a working electrode, a saturated Ag/AgCl electrode used as a reference electrode and a platinum electrode used as the auxiliary electrode. All measurements were carried out at room temperature.

2.3. Preparation of TmHCF modified glassy carbon electrode (GCE)

The TmHCF modified GCE was prepared by an electrodeposition method using a CV technique. To prepare the star fruit-like TmHCF modified GC electrode, first GCE was polished with alumina on polishing cloth followed by washing in DD water and ethanol. The polished GCE was placed in 5mM TmCl₃.H₂O and K₃Fe(CN)₆ in containing 0.1M KCl electrolyte. 20 consecutive cyclic voltammogram scans were performed between a potential range of 0.8 and -0.2 V at a scan rate of 50 mVs⁻¹. The star fruit-like TmHCF were electrochemically deposited on the GCE surface. Then, the TmHCF modified GCE was rinsed with water and dried at room temperature. Thus, the fabricated GCE was used for further electrochemical studies.

3. RESULTS AND DISCUSSION

3.1. Electrochemical deposition of TmHCF

TmHCF was synthesized by using a simple method of cyclic voltammograms electrochemical deposition is shown in Fig. 1. The uniform deposition of TmHCF on the GCE surface confirmed due to the presents of redox peak. The peaks at +0.2 and 0.33 V implies the reduction of Fe (CN)₆³⁻ and the corresponding peaks at +0.28 and 0.5 V with decreasing currents in the redox couple implies the oxidation reaction of the Fe(CN)₆³⁻ in the solution. The Tm³⁺ ions presents in the solution eagerly react with Fe (CN)₆⁴⁻ ions and deposited on the electrode surface, the second redox couple indicates the reduction process of Tm[Fe (CN)₆] is the contribution to the deposition of K[TmFe(CN)₆] on the electrode surface. The formation of TmHCF mechanism can be expressed as follows; [26-30]

\[
\text{Fe (CN)₆}^{3⁻} + e^- \rightarrow \text{Fe (CN)₆}^{4⁻} \quad (1)
\]

\[
\text{Fe (CN)₆}^{4⁻} + \text{Tm}^{3⁺} + K^+ \rightarrow \text{K[TmFe (CN)₆]} \quad (2)
\]

To investigate the deposition process, using the equal amount of (5 mM) thulium and hexacyanoferrate containing 0.1 M KCl solution at the cycle deposition between 0.8 to -0.2 V at a scan
rate of 50 mV s\(^{-1}\). On other hand, for the different amount no redox peak observed, but if the potential change, the redox peak may be appear faintly (figures not shown). The optimal amount of MHCF deposition was found only for 5 mM metal precursor which enhances the reversible process during the deposition and the same concept was used in this study.

**Figure 1.** Electrodeposited TmHCF modified electrode in 0.1 M KCl solution containing 5 mM TmCl\(_3\).6H\(_2\)O and K\(_3\) Fe(CN)\(_6\) solution. CV curves were recorded for 20 cycles consecutives between 0.8 to -0.2 V at scan rate of 50 mVs\(^{-1}\).

3.2. **Surface morphology of TmHCF**

**Figure 2.** Surface morphology of TmHCF using SEM at different magnification images (A-C), SEM affiliated EDX spectrum (D).
Surface morphology of TmHCF was analyzed by SEM and SEM affiliated EDX spectra. The star fruit like TmHCF was deposited at cyclic voltammograms using 20 consecutive cycles and the different number of cycles were carried out during the deposition to confirm the growth of TmFe(CN)$_6$ on the surface of GCE. The TmHCF were observed with star fruit-like structure, which shown in Fig. 2. Moreover, the SEM affiliated EDX spectrum confirmed the presence of TmFe(CN)$_6$ and give the weight percentage of constituents in TmFe(CN)$_6$. Here the Tm weight % of 57.71, Fe weight % of 12.08, potassium weight % of 7.20. These results were recorded on TmFe(CN)$_6$ deposited ITO surface.

3.3. Different electrolyte deposition for TmHCF

To investigate the morphological changes according to the nature of the electrolyte, the GCE placed in different types of electrolytes such as 0.1 M KCl, HCl, LiCl and NaCl during the deposition process. The different morphologies of TmHCF were observed for corresponding electrolytes and shown Fig. 3 (A-D). From the SEM images KTmHCF were observed clearly as star fruit-like structure as shown in Fig. 3 (A). The unequal size of cubic and spherical like structures were observed for HTmHCF and the fewer amounts of particles were deposited on the modified electrode surface as shown Fig. 3 (B). Moreover, the unequal size of particles and star like structures for LiTmHCF as shown Fig. 3 (C) and the star-like structure for NaTmHCF shown in Fig. 3 (D). Here, the LiTmHCF and NaTmHCF are deposited on the GCE surface with fewer amounts of particles only. Further, the H$^+$, Na$^+$, and Li$^+$ electrolyte was observed in the particle size, shape, stability and electrochemical properties for few parts only. The uniform morphology changes observed in the order of K$^+>$Na$^+>$Li$^+>$H$^+$. Hence, in this work K$^+$ electrolyte was used to obtain the well uniform morphology and for all further experiment.

Figure 3. The effect of different electrolyte such as 0.1 M (KCl, HCl, LiCl and NaCl) studies was used by SEM images (A-D).
3.4. XRD and EIS Characterization of star fruit like TmHCF

In the X-ray diffraction pattern the Fig. 4 (A) shows the major peaks with corresponding crystal planes (211), (222), (400), (440) and (640) for the TmHCF film. The result indicates that Tm$^{3+}$ ions are successfully deposited on the ITO plate. The electrochemical impedance spectroscopies (EIS) carried out to determine the electron transfer behavior of TmHCF modified electrode. From the Nyquist plot and Randles circuit the real component ($Z_{re}$) and imaginary component ($Z_{im}$), charge transfer resistance ($R_{ct}$), solution resistance ($R_s$) and capacity ($C_{dl}$) were obtained for TmHCF modified GC electrode. The $R_{ct}$ value obtained for bare GCE of about 138.6 Ω. Then, the $R_{ct}$ value for TmHCF modified GC electrodes of about 713.68, 661.71, 363.84, 316.54 Ω by varying the number deposition cycles 5, 10, 15, and 20 respectively is shown in Fig. 4 (B). Finally, the low charge transfer resistance $R_{ct}$ obtained for 20 cycles.

Figure 4. (A) XRD pattern, (B) EIS Spectrum analysis of different modified electrode by using 0.5 M KCl solution in containing 5 mM [Fe(CN)$_6$]$^{3/4-}$ electrolyte.
3.5. Electrochemical studies of TmHCF-GCE

Fig. 5 (A, C) shown the CV curve for TmHCF-GCE for both with and without of L-Cysteine (145 µL) in a 0.5 M KCl solution at a different scan rate of 50-500 mVs\(^{-1}\). The inset in fig. 5 (A, C) shown the linear calibration plot for the square root of scan rate vs current. The linear regression equation were calculated to anodic and cathodic value of with presents \(R^2 = 0.9869, 0.9677\) and without presents of \(R^2 = 0.9914, 0.9989\). Here, the increasing current values were observed with increases scan rates and also the peaks potentials were shifted to positive side. The result implies the kinetic of overall process were controlled by diffusion process.

**Figure 5.** CV curves of different scan rate from 50-500 mVs\(^{-1}\) at the without and with presents of (145 µM) L-cysteine (A, C) (inset: the corresponding calibration plots were calculated by the square root of scan rate vs current). CV curves of film comparison for (a) bare GCE only, (c)blank of TmHCF-GCE, (b) bare GCE, (d) TmHCF-GCE at the presents of (145 µM) L-cysteine, (B). CV Curves of different addition to L-Cysteine (inset: the corresponding calibration plot was calculated by different concentration of l-cysteine vs current). All experiments were during the 0.5 M KCl electrolyte at N\(_2\)-saturated.
CV curves for film comparison of the different electrode were studied by a 0.5 M KCl solution of L-Cysteine (145µL) at a scan rate of 50 mVs\(^{-1}\), as shown in fig. 5 (B). (a) bare GCE, (c) TmHCF-GCE with absence of L-cysteine, (b) bare GCE and (d) TmHCF-GCE with presents of L-Cysteine (145µL) in 0.5 M KCl solution at a scan rate of 50 mVs\(^{-1}\). Here, TmHCF-GCE shows the better redox response for L-cysteine than bare GCE. Fig 5 (D) shown the CV curves of TmHCF-GCE electrode for varying the concentration of L-cysteine with increasing redox current. The linear calibration plot was calculated for different concentration \(\text{vs} \) current. The linear calibration value were determined of about \(R^2 = 0.9948\).

3.6. DPV studies of TmHCF-GCE

The TmHCF-GCE were studied by a DPV curves with increasing the concertation of L-cysteine in \(N_2\) saturated 0.5 M KCl electrolyte at scan rate of 50 mV s\(^{-1}\), as shown Fig. 6. The inset shows the corresponding calibration plot for different concentration \(\text{vs} \) current. The linear calibration plot with the value of \(R^2 = 0.9837\) and the linear range were observed from 0.5 to 8.92 µM. the Low detection limit and sensitivity were calculated to be 16 nM and 48.479 µA µM\(^{-1}\) cm\(^{-2}\), respectively. The obtained results were compared with previously reported literature and shown in table 1.

![Figure 6. DPV curves of different concentration of L-cysteine for 0.5 M KCl electrolyte at \(N_2\) saturated at the scan rate of 50 mV s\(^{-1}\) (inset: the corresponding calibration plot was calculated by using different concentration \(\text{vs} \) current).](image)

3.7. Repeatability, reproducibility and stability

The repeatability of the TmHCF-GCE modified electrode for L-Cysteine sensor was observed from CV measurements in the same electrolyte conditions. The as prepared modified electrodes exhibit
good repeatability with a relative standard deviation (RSD) of three following measurements. Here, the modified electrode was observed excellent reproducibility of the RSD value 4.4% for three individual electrode measurements. The modified electrodes show better stability in the same 0.5 M KCl electrolyte solution. The constant oxidation peak current obtained for the modified electrode towards sensing of L-Cysteine for the two consecutive days and the 91% of peak current remain same for one weeks (figure not shown), which is showing an exceptional storage stability TmHCF-GCE modified electrode.

Table 1. Comparison of different modified electrodes for the detection of L-Cysteine.

<table>
<thead>
<tr>
<th>Modified electrodes</th>
<th>Techniques</th>
<th>LOD (µM)</th>
<th>Sensitivity (µA µm⁻¹cm²)</th>
<th>Linear range (µM)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–CoHCF</td>
<td>CV</td>
<td>4</td>
<td>-</td>
<td>6-1000</td>
<td>31</td>
</tr>
<tr>
<td>MWCNT-FeTsPc/GCE</td>
<td>Amperometry</td>
<td>1</td>
<td>0.176</td>
<td>10-200</td>
<td>32</td>
</tr>
<tr>
<td>Q–AgNPs–GNs–GCE</td>
<td>DPV</td>
<td>0.28</td>
<td>-</td>
<td>0.9-12</td>
<td>33</td>
</tr>
<tr>
<td>PPy/GQDs@PB/GF</td>
<td>Amperometry</td>
<td>0.15</td>
<td>0.4</td>
<td>50-1000</td>
<td>34</td>
</tr>
<tr>
<td>YHCF NP/MWNT/Nafion</td>
<td>Amperometry</td>
<td>0.16</td>
<td>0.1015</td>
<td>0.20-11.4</td>
<td>35</td>
</tr>
<tr>
<td>MoS₂/PDDA-MC/GCE</td>
<td>Amperometry</td>
<td>0.090</td>
<td>-</td>
<td>0.45-155</td>
<td>36</td>
</tr>
<tr>
<td>[PEI/PSS]₂/Au@2Ag/[PEI/P₂Mo₁₁V₂]/ITO</td>
<td>Amperometry</td>
<td>0.027</td>
<td>1.7946</td>
<td>0.025-7.6</td>
<td>37</td>
</tr>
<tr>
<td>TmHCF/GCE</td>
<td>DPV</td>
<td>0.016</td>
<td>48.479</td>
<td>0.5-8.92</td>
<td>This work</td>
</tr>
</tbody>
</table>

3.8 Real sample analysis

Table 2. Real sample analysis with TmHCF-GCE.

<table>
<thead>
<tr>
<th>Real samples</th>
<th>Analyte</th>
<th>Added (µM)</th>
<th>Found (µM)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human urine</td>
<td>L-Cysteine</td>
<td>20</td>
<td>19.5</td>
<td>97.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>49.1</td>
<td>98.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>58.7</td>
<td>97.81</td>
</tr>
<tr>
<td>River water</td>
<td>L-Cysteine</td>
<td>50</td>
<td>49.01</td>
<td>98.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>141.5</td>
<td>99.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>291.06</td>
<td>97.02</td>
</tr>
</tbody>
</table>

The TmHCF-GCE was tested in the real sample analysis in urine and river water samples by using the standard addition method. The L-cysteine was contained in the urine sample within the ranges of 0.03-0.3 mmol/24h. The different addition of urine sample was added in TmHCF-GCE and the results shown in table 2. Furthermore, the same experiment was carried out in the river water
samples and its corresponding results also given (table 2). Hence, the modified electrode is well detected in the real sample.

4. CONCLUSIONS

In this report, star fruit-like TmHCF was successfully synthesized in electrochemical deposition by using cyclic voltammetry technique. The star fruit like TmHCF-GCE found as the promising electrode for L-cysteine sensor. The nature of different electrolyte has played an important role to obtain the different morphology of TmHCF during the deposition which is confirmed by SEM. The crystallinity and the presents of constituents were determined using XRD and SEM affiliated EDX. Finally, the electrochemical activity such as sensitivity, low detection limit and linear range of TmHCF-GCE towards L-cysteine probed using CV and DPV technique.

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Reference

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