A Sol-gel Derived Surface Modified CuHCF Nanoparticles Carbon Ceramic Composite Electrode and Its Application for Hydrazine Determination

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Abstract: An amperometric sensor for hydrazine determination was developed using a surface modified copper (II) hexacyanoferrate (CuHCF) nanoparticles carbon ceramic composite electrode (CCE) by a versatile sol-gel technique using aminopropyl trimethoxysilane (APTMOS). The characterization of the modified electrode has been carried out by electrochemical techniques such as cyclic voltammetry, hydrodynamic voltammetry and Chronoamperometry. The cyclic voltammograms of the modified CuHCF nanoparticles-CCE prepared under optimum composition, showed a well-defined one-electron redox couple due to Fe(CN)₆⁴⁻/Fe(CN)₆³⁻ system with the formal potential of 0.68V (vs. SCE). This modified electrode exhibited electrocatalytic activity towards the oxidation of hydrazine at a reduced over potential with good sensitivity of 0.738 µA/µM in the wide concentration range 1.3 x 10⁻⁷ to 6.5 x 10⁻³ M and with a detection limit of 4.3 x 10⁻⁸ M. The proposed modified electrode exhibited the advantage of simple preparation, fast response, good stability and reproducibility for hydrazine determination. This modified electrode was successfully applied to the determination of hydrazine in boiler water samples and acceptable results were obtained.

Keywords: Sol-gel; Copper hexacyanoferrate; Modified electrode; Amperometric determination; Hydrazine

1. INTRODUCTION

There is an increasing demand for simple, inexpensive and rapid analytical tests to determine the concentrations of biological and environmental compounds. In recent years, modification of electrode surfaces with various electroactive materials is an interesting area of research in designing electrochemical sensors.

A major attention has been focused on the development of chemically modified electrodes during the last two decades. The application of chemically modified electrodes (CMEs) offer significant advantages in the design and development of electrochemical sensors, in which the working electrodes have been achieved through judicious surface modifications with various redox mediators, which facilitate charge transfer between the electrode and an electroactive species in solution at much lower potentials than would otherwise be possible [1-3]. Transition metal hexacyanoferrates (MHCFs) is one of the important groups of inorganic compounds utilized for electrode modification and used for electrocatalytic purposes containing specifically selected redox mediators immobilized at chemically modified electrodes which offer a promising approach for minimizing overvoltage effects [4].

Sol-gel chemistry offers new and interesting possibilities in the fields of chemical sensors and biosensors. The silica based gel approach has demonstrated some benefits by using a ceramic as binder in the fabrication of carbon ceramic composite electrodes. They are made of a continuous robust silica background entrapping interconnected carbon particles to impart electronic conductivity. Their preparation involves the dispersion of carbon powder within silica sol that is then allowed to jellify and to dry. They are more robust than carbon paste electrodes and do not require any organic binder, because the compactness is ensured by the silicate continuum. Besides, they can be obtained in various configurations and organic and inorganic species [5-7] as well as biological molecules [8,9] are usually introduced into CCEs via either adsorption on graphite particles or direct entrapment during the sol-gel process. Among the most important requirements to make a carbon ceramic composite suitable for use as an electrode material are those related to chemical composition, electrical conductivity, and stability under repeated electrochemical cycling. These features mostly depend on the chemical and electrical nature of the silica matrix.

Hydrazine, a colorless liquid compound, is expected to be a human carcinogen [10-12]. This substance is a powerful reducing agent and is widely employed in many industrial applications as reagent, catalyst and corrosion inhibitor. Because this substance (and its derivatives) is applied in such a variety of different fields and has been recognized as carcinogenic and hepatotoxic agent [13,14], its quantitative determination is of great importance.
analytical importance attracting the interest of many researchers [15]. Various chemically modified electrodes have been applied in the determination of hydrazine, including cobalt phthalocyanine modified carbon paste electrodes [16], oxymanganese film-modified electrodes [17], platinum particles-modified carbon fiber microelectrodes [18], chlorogenic acid modified glassy carbon electrodes [13], cobalt pentacyanonitrosylferrate glassy carbon electrode [19], CCEs modified by NiHCF [20-22] and bismuth hexacyanoferrate [23].

In the present study the fabrication, stability and electrochemical properties of CuHCF nanoparticles modified carbon composite electrode was investigated. As transition metal ions such as Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$ posses a greater affinity towards amines, Cu$^{2+}$ was coordinated to the amine group of APTMOS which was used for preparing CCE followed by derivatising the coordinated metal ion to its stable hexacyanoferrate as a film on the surface of the electrode. The proposed CuHCF nanoparticles modified electrode fabricated using a sol-gel method surpasses the sensitivity achieved by a mechanically immobilized nickel hexacyanoferrate modified paraffin impregnated electrode and manganese hexacyanoferrate modified composite electrode for hydrazine determination [11, 24]. The resulting CME was shown to exhibit an excellent electrocatalytic response toward the oxidation of hydrazine at reduced potential with good sensitivity and stability. The fabrication process was found to be simple, reproducible, cost effective and the sensor exhibits good sensitivity and reproducibility for the determination of hydrazine.

2. EXPERIMENTAL

2.1 Materials and Reagents

3-Aminopropyltrimethoxysilane (APTMOS), Methyltrimethoxysilane (MTMOS), high purity graphite powder (1-2 µm) and hydrazinium chloride were purchased from Aldrich chemicals, USA. Copper (II) chloride, potassium ferrocyanide, potassium nitrate and all other reagents were of analytical grade unless otherwise specified. The working solutions of hydrazinium chloride were prepared freshly each day from the stock solution. All aqueous solutions were prepared using double distilled water. Electrochemical experiments were conducted in 0.1 M KNO$_3$ solution. The pH of the solution was adjusted using 0.1 M HNO$_3$ and 0.1 M KOH solutions. Phosphate buffer (0.05 M) was used when the pH was maintained at 7. All measure-ments were done after carefully degassing the solutions with pure nitrogen. Samples of water from hot-water heating systems was obtained from Malladi Drugs and Pharmaceuticals Ltd, Ranipet, Tamilnadu, India and spiked with hydrazine (0.50 mg/L). The boiler water was found to have no hydrazine content on preliminary analysis.

2.2 Instrumentation

Electrochemical measurements were done using a CHI 400A Electrochemical Analyzer (CH Instruments, USA) interfaced to an IBM personal computer with standard three-electrode configuration. A surface modified CuHCF nanoparticles-CCE as the working electrode, a platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode were used. All electrochemical experiments were carried out in a cell of volume of 60 mL at room temperature (25-30°C) under nitrogen atmosphere. A magnetic stirrer and a Teflon coated stirring bar provided the convective transport during the amperometric studies. Elico pH meter (Model LI 120) was used for checking pH of the solutions.

2.3 Fabrication of CuHCF Nanoparticles Modified CCE

The CuHCF nanoparticles modified CCE was prepared by thoroughly mixing a solution of 0.4 mL APTMOS, 0.6 mL of MTMOS, 0.6 mL of methanol and 20 µL HCl (10 mM) for 5 min until a homogeneous sol-gel solution was obtained. Then, 0.8 mL of homogenous sol-gel solution was added to 0.550 g of graphite powder and the resultant mixture was thoroughly mixed for an additional of 1 min. Subsequently a suitable amount of the composite mixture was tightly packed immediately into a 3mm diameter glass tube (5 cm long) and the composite electrode was gently removed and dried at room temperature. The electrode was polished on polishing paper first to remove the extra composite and then on weighing paper until shiny surface was obtained. The electrode surface was dipped in 0.01 M CuCl$_2$ solution for 3 min. The electrode was then thoroughly washed with ethanol followed by doubly distilled water. The Cu$^{2+}$ ions coordinated to the amine on the graphite surface is then derivatised to CuHCF nanoparticles film by cycling with potassium ferrocyanide (0.02 M) dissolved in 0.1 M KNO$_3$ solution in the potential range – 0.2 to 1.0 V for 15 cycles. Similarly an electrode without dipping its surface in 0.01 M CuCl$_2$ solution was used as the bare electrode. Schematic representation of the entire fabrication approach of CuHCF nanoparticles modified electrode is shown in Scheme 1.

Scheme 1: Schematic Representation of the Entire Fibrication Approach of CuHCH Nanoparticles Modified Electrode
3. RESULTS AND DISCUSSION

3.1 SEM

Scanning electron microscopy (SEM) was employed to gain insights into the surface morphology of the CuHCF nanoparticles modified CCEs. The SEM images presented in Figure 1 shows the surface of the modified CCE, As this figure shows the size of CuHCF nanoparticles is almost between 60-75nm.

![SEM Image of CuHCF Nanoparticles Modified Electrode](image)

3.2 Electrochemical Characterization of CuHCF Nanoparticles Modified CCE

The voltammetric characteristics of CuHCF nano-particles modified electrode, including redox potential, voltammetric wave shape and peak currents, are dependent on the cations being incorporated inside the lattice [25]. To maintain the electro neutrality of the metal hexacyanoferrate modified electrode, it is important to equilibrate the compounds with the electrolyte by repeated oxidation and reduction, because the starting compounds may contain metal ions in their channels from the synthesis, which must be excluded from lattice to the solution by potential scanning. The electrochemical behavior of CuHCF nanoparticles modified CCE was studied using 0.1 M KNO₃ (scan rate of 20mV/s). It was observed that the modified CCE after cycling through potential window -0.2 to 0.9 V showed reproducible cyclic voltammograms which is shown in Figure 2. The modified electrode exhibits a pair of redox peaks at a formal potential (E (Ep_a+/Ep_c))/2 of 650 mV vs reference electrode (E_p = 60mV and I_p/I_r was almost equal to 1). These peaks can be attributed to the reversible redox reaction of Fe⁺⁺ to Fe⁺⁺⁺ in CuHCF nanoparticles. We observed that this peak is not affected by stirring of the electrolyte, offering proof that the material is well associated with the electrode surface under the solution conditions and no obvious changes in the peak current and the peak potential values were observed for more than 100 cycles, which indicate the good stability of the electrode.

![Cyclic Voltammograms of (a) Bare CCE and (b) CuHCF Nanoparticles-CCE at a Scan Rate of 20 mV/s in 0.1 M KNO₃](image)

3.3 Effect of Cation and Anion of Supporting Electrolyte

The effect of alkali metal cations towards the voltammetric behavior of the CuHCF nanoparticles modified CCE was investigated by changing the cation in the electrolyte solution. The electrochemical response of the CuHCF nanoparticles modified electrode in the presence of different cations such as K⁺, Li⁺, Na⁺, NH₄⁺, Cs⁺ of the same concentrations is shown in Figure 3. The results showed that well-defined voltammograms are obtained in the presence of K⁺ ions indicating that the K⁺ ion can freely penetrate the CuHCF nanoparticles lattice. During the electrochemical process, the film must maintain its electroneutrality; cations usually enter or leave the CuHCF nanoparticles film during redox reaction, so these ions have a considerable effect on the electrochemical behavior of the modified electrodes. The length of the edge of the unit cell and the diameter of the cage for CuHCF nanoparticles are 1.0 and 0.32 nm respectively and K⁺ ion have a hydrated diameter of 0.24 nm and hence can easily fit well within the cage to allow for generation of faradic current upon electrochemical cycling. As the hydrated diameter of other cations are higher than the zeolite cage diameters, their movement is restricted and hence the redox behavior of CuHCF nanoparticles modified electrode was not well defined and also less stable in presence of other cations. Further, the performance of the CuHCF nanoparticles modified electrode with different anions such as Cl⁻, NO₃⁻ and SO₄²⁻ was also examined. From the cyclic voltamograms (figure not shown), the electrochemical behavior of the modified electrode was found to be independent of the nature of anions. As well defined redox peaks and higher currents were obtained in KNO₃ medium, hence further experiments were carried out using 0.1M KNO₃ as the supporting electrolyte. The electrochemical reaction of the redox couple can be expressed as follows:

\[ \text{M Cu Fe}^{\text{II}}(\text{CN})_6 \rightarrow \text{CuFe}^{\text{III}}(\text{CN})_6 + \text{M}^+ + e^- \quad (1) \]
Where $M = (K^+, Li^+, Na^+, NH_4^+, Cs^+)$, Eq. (1) implies the direct involvement of counter cation in the redox process of CuHCF nanoparticles.

Figure 4 shows the cyclic voltammograms of CuHCF nanoparticles - modified CCE electrode in a 0.1 M KNO$_3$ solution at different scan rates (in the range 25–250 mV/s). The peak currents were proportional to the square root of the scan rate which can be expected for a diffusion-controlled electrode process (Inset Figure 4) and the ratio of anodic and cathodic peak currents for different scan rates is almost unity. This implies that the diffusion of electrolyte ions into and out of the CuHCF nanoparticles lattice is essential for charge compensation during redox process. The peak to peak separation, $E_P$, was only about 60 mV at a scan rate of 20 mV/s indicate excellent electrochemical reversibility at this scan rate. The surface coverage can be evaluated from the equation $\frac{Q}{nFA}$, where Q is the charge obtained by integrating the anodic peak (at a low scan rate of 20 mV/s), $A$ is the electrode area (cm$^2$), $n$ is the surface coverage of the electroactive substance (mol cm$^{-2}$) and other symbols $n$, $I_p$, $F$, $R$, $T$ have their usual meanings. Now by assuming the involvement of one electron in the process, the calculated value of $9.83 \times 10^{-9}$ mol/cm$^2$.

3.4 Effect of the pH Solution

The effect of pH on CuHCF nanoparticles modified CCE in a 0.1 M KNO$_3$ solution as a supporting electrolyte was studied over the pH range of 2-9 by cyclic voltammetry. The dependence of the peak current and peak potential of the electrode was examined by varying the pH of the electrolyte (0.1M KNO$_3$) using KOH and HNO$_3$. This study showed that the peak current and peak potentials of the CuHCF nanoparticles modified CCE did not change appreciably in the pH range 2-8, but decreased in basic medium (pH higher than 9), indicating a gradual disintegration of the CuHCF nanoparticles film by hydrolysis (Figure 5). The poor response at very high acidic and basic could be due to the dissolution of the mediator [21]. The possible reason for poor response at higher pHs may be due to the hydrolylation of the CuHCF nanoparticles film in alkaline medium as given below:

$$[Fe(CN)_6]^{4+} + 2OH^- \rightarrow Fe(OH)_2 + 6CN^-$$
$$2Fe(OH)_2 + H_2O + 1/2 O_2 \rightarrow 2Fe(OH)_3$$

Therefore, the utility of the modified electrode is limited to neutral and weakly acidic solutions. This observation is similar to the reported method [26].

3.5 Electrocataytic Oxidation of Hydrazine

The electrocatalytic activity of the CuHCF nanoparticles modified electrode towards the oxidation of hydrazine was studied by cyclic voltammetry. The CuHCF nanoparticles modified showed excellent electrocatalytic activity towards the oxidation of hydrazine. Results show that the anodic peak current increases with
increasing hydrazine concentration in the range of $1.3 \times 10^{-7}$ to $6.5 \times 10^{-3}$ M and the cathodic peak current decreases. The anodic current enhancement in the presence of the analyte can be attributed to the oxidation of hydrazine by ferricyanide formed on the electrode surface during anodic scanning. When compared to bare electrode a large decrease in overpotential (about 550 mV) and enhancement of peak current for hydrazine oxidation was achieved with the modified electrode. In Fig. 6 curve (a), shows the CV of bare CCE at pH 7, Curve (b), shows the CV of the bare CCE in the solution containing $9.1 \times 10^{-4}$ M hydrazine. There is no obvious peak corresponding to oxidation of hydrazine on the surface of bare electrode (curve b). Curve (c) is the background current of CuHCF nanoparticles-modified CCE at pH 7 and Curve (d) is the CV of the same electrode in the presence of $9.1 \times 10^{-4}$ M hydrazine. Clearly, the CuHCF nanoparticles-modified CCE has the significant catalytic effect on the oxidation of hydrazine. As is shown, the oxidation current of hydrazine on the surface of modified electrode is significantly increased and the corresponding oxidation potential is shifted toward negative potential values. The CV of hydrazine at the bare CCE exhibit a short peak at the potential of 0.8 V, while at the CuHCF nanoparticles-modified CCE the peak current is enhanced significantly with a sharp signal at the 0.68 V. The result of the reduced over potential and increase current response are the clear evidence for the catalytic effect of the CuHCF nanoparticles film present on the electrode. From the above results the catalytic oxidation of hydrazine at the CuHCF nanoparticles modified surface can be represented in the following scheme (Scheme. 2).

3.6 Hydrodynamic Voltammetric Studies of Hydrazine at a CuHCF Nanoparticles Modified CCE

Hydrodynamic voltammetric experiments were performed with the CuHCF nanoparticles modified electrode to investigate its electrocatalytic response under dynamic conditions. To optimize the working potential, the dependence of the hydrazine response on applied potential was studied in the potential range from -0.2 to 0.9 V. The current response was measured as a function of applied potential. Figure 7 shows hydrodynamic voltammograms for the oxidation of $9.1 \times 10^{-4}$ M hydrazine at the bare and modified electrodes. The voltammograms were plotted by measuring the current response in stirred solution. The bare electrode does not permit a convenient quantification of hydrazine. In contrast, CuHCF nanoparticles modified CCE exhibits a well-defined response showing distinctly sigmoidal voltammograms with a plateau starting at 0.68 V. This confirms the result obtained in CV experiments and allows convenient monitoring of hydrazine at lower potentials, thus minimizing interference and background current. A potential of 0.68 V can be selected for the determination of hydrazine in a chronoamperometric measurements.

3.7 Chronoamperometric Studies

Amperometric response of the CuHCF nanoparticles modified CCE for hydrazine determination was examined in 0.1 M KNO₃ by measuring the catalytic current at a potential of 0.68 V vs. SCE. Figure 8 shows the typical amperograms during the successive addition of 0.5 mL of 10 mM of hydrazine into continuously stirred 60 mL of 0.1 M KNO₃ solution at 300 rpm. For repeated additions of hydrazine this electrode gave a sharp increase in current and attains a steady state condition.
In chronoamperometric studies, the diffusion coefficient of hydrazine for the modified electrode can be determined. The relationship between diffusion coefficient and bulk concentration can be described by the Cottrell equation [27]:

\[ I = nFAD^{1/2}/C^{1/2}t^{1/2} \]

where \( D \) and \( C \) are the diffusion coefficients (cm\(^2\)/s) and the bulk concentration (M), respectively. In addition, the level of the current, which was measured for 60s, increases with increasing concentration of hydrazine. From the equation it can be seen that the plot of \( I \) vs. \( t^{1/2} \) is linear, and from the slope, the value of \( D \) can be obtained. The response of the electrode is linear over the concentration range of 1.3 × 10\(^{-7}\) to 6.5 × 10\(^{-3}\) M. From the regression analysis of the CuHCF nanoparticles-CCE, a slope of 0.738 µA/µM and a correlation coefficient of 0.9930 were obtained. The electrode has a detection limit of 4.3 × 10\(^{-8}\) M at a signal to noise ratio (S/N) of 3. The electrode response time was less than 2 s. A calibration curve was recorded in a 0.1 M KNO\(_3\) solution containing hydrazine with a concentration between 2 and 21 µM. The response is linearly proportional to the concentration of hydrazine (Fig. 8). The above results indicate the fact that CuHCF nanoparticles modified electrode shows a lower detection limit and is very sensitive for hydrazine determination. One of the advantages of this modified electrode for the amperometric determination of hydrazine is its highly stable amperometric response during longer periods. These experiments indicate that the catalytic hydrazine oxidation at the CuHCF nanoparticles modified electrode prepared by sol-gel technique is very promising for the fabrication of stable and highly sensitive sensor for hydrazine determination.

### 3.8 Interference Studies

The influence of various species for the determination of hydrazine (0.1 mM) was studied under optimized conditions. The tolerance limit was defined as the maximum concentration of interfering species that cause an error less than 4% for determination of 0.1 mM hydrazine. The results presented in Table 1 are in agreement with previous report [10] and show very good selectivity for the proposed electrode.

#### Table 1

Results of interference study for the determination of 0.1 mM hydrazine under optimized conditions

<table>
<thead>
<tr>
<th>Interference species</th>
<th>Maximum tolerable concentration ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(^-), Br(^-), F(^-), Na(^+), K(^+), NH(_4^+)</td>
<td>1000</td>
</tr>
<tr>
<td>CH(_3)COO(^-), CO(_2)(^2-), NO(_2^+)</td>
<td></td>
</tr>
<tr>
<td>NO(_3^+), PO(_4^3-), SO(_4^2-)</td>
<td></td>
</tr>
<tr>
<td>glucose, fructose, lactose</td>
<td></td>
</tr>
<tr>
<td>CO(_3^2-), Ba(^{2+}), Mg(^{2+}), Ca(^{2+})</td>
<td>100</td>
</tr>
</tbody>
</table>

### 3.9 Reproducibility and Long-term Stability Response of Modified CCE

The stability of the CuHCF nanoparticles modified CCE was investigated by cyclic voltammetry. The working stability of the modified electrode was verified by monitoring the remaining amount of active substance after successive sweeps of cyclic voltammograms (Fig. not shown). The peak current and peak potential of the modified electrode, by cycling the electrode over the potential range 0.2–0.9 V, remained nearly unchanged. The amount of CuHCF nanoparticles remaining on the electrode surface is almost 96% after 200 cycles in electrolyte solution with a scan rate 20 mV/s. On the other hand the storage stability of the chemically modified electrodes was very good, as the electrodes were found to have reserved (97%) their initial activity for more than 4 months when kept in air at room temperature. The high stability of the modified electrode is related to the chemical and mechanical stability of the silicate matrix, the limited wetting section controlled by methyl group, the strong adsorption of CuHCF nanoparticles on graphite powder and the possible interaction between the CuHCF nanoparticles and silanol groups.

### 3.10 Analytical Application

The CuHCF nanoparticles-CCE was used as amperometric detection system for the application in analysis of hydrazine. The developed method was applied to the determination of hydrazine in boiler water samples spiked with 0.50 mg/L of analyte and were analyzed under optimized conditions using the above technique. The determination of hydrazine was carried out by applying the standard additions method to avoid matrix
effects and the concentration in the analytical solution was $2.0 \times 10^{-5}$ m/L. Results obtained from 10 different analyses yielded a mean recovery of 100 ± 3%, indicating that the method is suitable for the determination of hydrazine in this type of samples.

4. CONCLUSIONS
The results of the above study confirm that the CuHCF nanoparticles modified carbon ceramic composite electrode fabricated using sol-gel technique proves to be an excellent amperometric sensor for the determination of hydrazine. The CuHCF nanoparticles modified CCE shows very good catalytic activity with good linearity for the hydrazine determination over a range of $1.3 \times 10^{-7}$ to $6.5 \times 10^{-3}$ M with a detection limit of $4.3 \times 10^{-8}$ M and a correlation coefficient of 0.9930 with a slope of 0.738 $\mu$A/$\mu$M. The hydrodynamic voltammetric result suggests that the modified electrode could be developed as a useful sensor for the on line monitoring of hydrazine in flow systems. The advantage of this method is the electrode fabrication, good stability, longer shelf life, low cost and its diverse application for hydrazine determination.

REFERENCES


