Camphor sulfonic acid surfactant assisted polythiophene nanocomposite for efficient electrochemical hydrazine sensor

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Abstract

In this present work, we demonstrate an efficient electrochemical sensor for the detection of hydrazine, using glassy carbon electrode (GCE) modified with camphor sulfonic acid (CSA) assisted polythiophene / aluminium oxide (PTHA) nanocomposite. The CSA-PTHA nanocomposite was synthesised using an in situ chemical oxidative polymerisation method. The nanocomposite was characterised by XPS, AFM, DSC / DTA and impedance analysis. The CSA-PTHA nanocomposite modified GCE can be used for efficient hydrazine electrochemical sensor with high sensitivity and low limit of detection (LOD). The electrochemical detection test of hydrazine was conducted with CSA-PTHA modified GCE by the cyclic voltammetry (CV) and amperometric techniques and the results are compared with pure polythiophene (PTH) modified GCE. Comparing with PTH modified GCE; CSA-PTHA modified GCE illustrates a higher sensing performance leading to significant sensitivity of $0.285 \, \mu A \, \mu M^{-1} \, cm^{-2}$ and a very low LOD of $0.18 \, \mu M$ at $S/N = 3$ for wide linear range of hydrazine concentration from $10 \, \mu M$ to $90 \, \mu M$ with a correlation coefficient $R^2 = 0.99668$. Also, the performance of CSA-PTHA modified GCE electrode is comparable or even better than that of the other reported functional materials for hydrazine detection. Hence, our result shows that the compositing of conducting polymer with metal oxide could offer an efficient way to fabricate advance and economic electrochemical sensors.

Introduction

Hydrazine and its derivatives are highly reactive chemicals that have been commonly used in several potential applications such as rocket propellants, fuel cells, insecticides, pharmaceutical, corrosion inhibitors, antioxidants, catalysts, emulsifiers and reducing agents [1–3]. However, hydrazine is extremely toxic and dangerously unstable compound unless it is handled in the form of solution and the long-term exposure of hydrazine causes various health problems in humans even if it is in low concentrations. Although material is important, it is reported as neurotoxin, hepatotoxic and carcinogenic [4]. Therefore, it is important to develop the precise detection techniques to measure the hydrazine level in the human body. Different sensing approaches for hydrazine detection such as chromatographic [5], spectrophotometric [6], chemiluminescence [7] and electrochemical techniques [8] have been developed. Among those techniques, the electrochemical technique has received much more attention because of their high sensitivity, rapid response, good selectivity and relatively low cost [9]. However, hydrazine determination from unmodified electrode suffers from poor sensitivity and also, the hydrazine oxidation requires a high overpotential and by-products that are usually accumulated on the electrodes [10]. A number of approaches were investigated to minimize the high over potential and increase the current response of hydrazine oxidation. One of the promising approaches is use of modified electrode with materials having favourable properties to overcome the disadvantages [11]. The hydrazine sensors based on metal oxide nanomaterials such as MnO$_2$, Co$_3$O$_4$, Fe$_3$O$_4$, CuO, and WO$_3$ have been intensively studied due to their large surface areas and unusual structural characteristics [12–15]. In particular, Al$_2$O$_3$ received much attention because it serves as a catalyst, absorbent, fire retardant, as well as filler for...
structural materials [16]. Although the metal oxide nanomaterials shows excellent catalysis towards hydrazine oxidation, the sensors fabricated using them often shows low sensitivity because of the intrinsic poor conductivity of metal oxide nanomaterials. Alternatively, metal oxide incorporated with conducting materials such as carbon nanotube or graphene is commonly used, in order to attain high sensitivity. However, carbon nanotube is expensive whereas graphene frequently suffers from irreversible aggregation and is difficult to synthesise. Therefore, it is essential to develop a new conducting material to support metal oxide nanomaterials for the fabrication of simple, high sensitive hydrazine sensors. Besides that, conducting polymers such as polyaniline, polypyrrole, polythiophene and its derivatives exhibits wide applications in electrochemical sensors [17]. Among these conducting polymers, polythiophene (PTH) is considered to be a favourable candidate as it has high electrical conductivity, easy to synthesise, outstanding thermal and environmental stability [18]. Currently, there is ample interest focused on combining metal oxides with conducting polymer to form a hybrid nanocomposite which shows an increased performance compared to their separate counterparts. These nanocomposites showed their excellent properties in different applications such as sensors, solar cell, supercapacitors and other organic electronics [19, 20]. M Faisal et al developed amperometric hydrazine sensor based on polythiophene/ZnO nanocomposite which shows much superior sensing performance than pure ZnO [21] and also F Kong et al [18] and W Feng et al [22] worked on hybrid nanocomposite materials for sensor applications and found that nanocomposites exhibit better sensing properties than the pure one. Hence, there is a vital need to fabricate a highly sensitive, fast response and consistent electrochemical sensors for early detection of hydrazine and there are very limited reports available on electrochemical sensors based on PTH and metal oxide hybrid nanocomposites [23–26]. This encouraged us to work on polythiophene hybrid nanocomposites.

In this present work, a new hydrazine electrochemical sensor is developed using GCE modified with PTH and CSA-PTHA nanocomposite synthesised by in situ chemical oxidative polymerisation method. The electrochemical sensing of hydrazine by PTH and CSA-PTHA was investigated using different techniques such as cyclic voltammetry and amperometric response. It was found that PTH shows poor catalysis for hydrazine oxidation whereas CSA-PTHA showed low overpotentials and great catalytic current for hydrazine oxidation. And also, the performance of CSA-PTHA modified GCE was similar or even superior to other previously reported functional materials for hydrazine sensors. To the best of our knowledge, this is the first study reporting the electrochemical sensor on CSA-PTHA nanocomposite for detection of hydrazine.

**Experimental techniques**

**Materials**

Thiophene monomer (99%), camphor sulfonic acid and hydrazine monohydrate were purchased from Sigma Aldrich. Aluminium oxide (Al₂O₃) powder, Ammonium persulfate (APS) (NH₄)₂S₂O₈, N-methyl Pyrrolidine (NMP) were purchased from Merck chemicals. Phosphate buffer solution (0.1 M, pH 7.4), prepared with sodium phosphate dibasic (Na₂HPO₄) and sodium monobasic (NaH₂PO₄) was used as supporting electrolyte. All the solutions used throughout the experiment were prepared with pure double distilled water (DDW).

**Synthesis of CSA-Polythiophene/Al₂O₃ nanocomposite**

The CSA assisted synthesis of PTHA nanocomposite was synthesised by in-situ chemical oxidative polymerisation of thiophene as reported earlier [27]. In this typical process, a saturation concentration with appropriate mass of Al₂O₃ (0.2 mg) was added to the round bottom flask containing CSA (0.01 mol) surfactant dissolved in 60 ml of DDW. APS (0.2 mol) is added to the above solution with continuous stirring for one hour. 0.1 mol thiophene monomer is dissolved in 60 ml DDW and the oxidant solution prepared above is added drop wise to this monomer solution. This suspension was heated for 24 h at 80 °C. The resultant brown coloured precipitate was collected and washed with methanol and DDW to eliminate unreacted monomers and impurities. Finally, attained CSA-PTH/(20%) Al₂O₃ (CSA-PTHA) nanocomposite was dried in oven for 24 h at 60 °C. The same procedure was followed for pure polythiophene (PTH) without adding Al₂O₃ powder.

**Characterization techniques**

The synthesised PTH and CSA-PTHA nanocomposite were characterised using various techniques. The chemical oxidation states of prepared sample was analysed by x-ray photoelectron spectroscopy (XPS) technique using Kratos Axis Ultra DLD under the condition of 13 mA emission current and 12 kV as accelerating voltage (156 W). Surface morphology of the nanocomposite was characterised using tapping mode atomic force microscopy (AFM) (Bruker dimension ICON). Thermal studies were carried out using Differential Scanning Calorimeter (DSC) and Differential thermal analysis (DTA) (Perkin Elmer STA 8000). Dielectric properties were studied using Agilent B1500A with pulsed source of 5 MHz.
Sensor fabrication and electrochemical characterisation
Prior to electrode modification, the glassy carbon electrode (GCE) was polished with alumina slurry of 0.5 μM followed by 0.05 μM and sonicated with water and ethanol. The cleaned and polished GCEs were then modified by coating it with PTH and CSA-PTHA active material with PVDF as a conducting binder, followed by drying at 60 °C for 5 h. A conventional three electrode setup with PTH, CSA-PTHA modified GCE as working electrode, platinum wire as counter electrode and Ag/AgCl (saturated KCl) as reference electrode was connected to CHI 660E electrochemical workstation. Various hydrazine concentrations ranging from 10–55 μM for PTH modified GCE and 10–90 μM for CSA-PTHA modified GCE were used in the experiments. For the detection of hydrazine, all the electrochemical measurements were conducted at room temperature and under constant magnetic stirring in 0.1 M PBS (pH 7.4) solution. All the electrochemical measurements were performed using CHI 660E electrochemical workstation.

Result and discussion
X-ray photoelectron spectroscopy
The surface level elemental oxidation states of the PTH and CSA-PTHA nanocomposite were characterised using XPS. Figure 1 shows the wide scan and high-resolution spectra of PTH and CSA-PTHA nanocomposite. The XPS wide scan spectrum indicates the presence of elements C, O, S and Al according to their respective binding energy in CSA-PTHA nanocomposite, whereas absence of element Al can be seen in pure PTH. The high-resolution C 1 s, O 1 s, S 2p and Al 2p spectral curves were fitted well with the Gaussian curves as shown in figures 1(a)–(d). The high resolution C 1 s spectrum was resolved into three peaks as shown in figure 1(a). The lower energy peak at 283.86 and 284.79 eV are arising from the aromatic α and β carbons of PTH. The peak at higher binding energy of 287.58 eV is referred to adventitious carbon. Figure 1(b) shows the high resolution O 1 s spectra. The peak at 530.66 and 532.16 eV were attributed to the oxygen in the Al–O and OH group respectively. The deconvoluted curve suggest that there are three S 2p spin orbital doublets, with the 2p3/2 peak centred at 163.63 eV and the lower binding energy peak at 162.60 eV (2p1/2) is attributed to sulphur in the thiophene [28].

And also, the lack of oxidised S 2p peak appearing at higher binding energy ~167.82 eV indicates that there is no S–O bonding [29]. The XPS Al 2p peak of CSA-PTHA nanocomposite is shown in figure 1(d). The Al 2p spectra can be deconvoluted into two peaks at 74.36 and 75.50 eV which are attributed to Al 2p3/2 and Al 2p1/2 respectively. The XPS result confirms the successful formation of CSA-PTHA nanocomposite.

Atomic force microscopy
The two dimensional (2D) and three dimensional (3D) surface morphology and roughness parameter of PTH and CSA-PTHA samples were investigated using AFM analysis, operated in tapping mode.

Three different factors were used to obtain the quantitative description from AFM images i.e. grain size, root mean square (RMS) roughness and average roughness (ARF). Figure 2(a)–(d) shows 2 μm × 2 μm AFM topographic images of PTH and CSA-PTHA nanocomposite having spherical structure with average grain size of 128 and 102 nm respectively. It was observed that the CSA-PTHA nanocomposite exhibits lower RMS (17.88 nm) and ARF (10.42 nm) value in comparison to that of the PTH (95.66 nm and 62.41 nm respectively). Higher RMS and ARF values obtained for CSA-PTHA nanocomposite is clearly show a smoother surface than the pure PTH.

Transmission electron microscopy
The microstructure of PTH and CSA-PTHA nanocomposite were characterised using transmission electron microscopy (TEM) technique. The TEM images of PTH shows irregular morphology which are closely interconnected to each other as presented in figures 3(a) and (d). The TEM images of CSA-PTHA shows irregular spherical shaped morphology and also, the metal oxide nanoparticles are encapsulated by the macromolecular PTH in a uniform manner as presented in figures 3(b) and (d). The formation of spherical shaped morphology indicates the intermolecular interaction between the nanoparticles and PTH. Also, the in situ polymerisation helps the thiophene monomer molecules to uniformly coat on the surface of nanoparticles. The average particle size of CSA-PTHA nanocomposite is found to be 138 nm. The selected area electronic diffraction (SAED) pattern of PTH and CSA-PTHA nanocomposite is shown in figures 3(c) and (f) respectively. The SAED pattern displays amorphous phase for PTH whereas CSA-PTHA nanocomposite shows crystalline phase due to good compositing with Al2O3 particles.
The phase transition in the PTHA nanocomposite was done by DSC analysis. Figure 4(a) shows the DSC curves of PTH and CSA-PTHA nanocomposite. It shows a broad endothermic transition from 115°C to 125°C, due to

**Figure 1.** XPS wide-scan (survey) spectra of Pure PTH and CSA-PTHA. The high-resolution scan spectra (Deconvoluted) of (a) C 1s, (b) O 1s, (c) S 2p and (d) Al 2p.

**DSC/DTA**
The phase transition in the PTHA nanocomposite was done by DSC analysis. Figure 4(a) shows the DSC curves of PTH and CSA-PTHA nanocomposite. It shows a broad endothermic transition from 115 °C to 125 °C, due to
Figure 2. AFM 2D and 3D images of (a & c) pure PTH (b & d) CSA-PTHA nanocomposite.

Figure 3. TEM image of (a) PTH (b) CSA-PTHA (c) SEAD pattern of PTH (d) CSA-PTHA nanocomposite.
the removal of monomers, water molecules and solvent molecules from the polymers [30]. The melting temperature of PTH and CSA-PTHA is found to be 109.35 °C and 125.18 °C respectively as shown in the figure 4(a). These results show the CSA-PTHA nanocomposite have high thermal stability than the PTH. The decomposition of the polymer starts at 340 °C up to 380 °C, because of deprotonation of the chains of polythiophene. The heat of fusion (ΔH) for PTH and CSA-PTHA are found to be 161.85 J g⁻¹ and 175.92 J g⁻¹, respectively.

The exothermic peak is observed at 536 °C for PTH whereas, the exothermic peak is shifted to lower temperature of 512 °C for CSA-PTHA nanocomposite, depicting the thermal decomposition of organic matters of the nanocomposite [31]. According to DTA plot thermal degradation occurs from 250 °C to 530 °C. The change in the DTA curve indicates the enhanced thermal stability in PTH due to the addition of surfactant and nanocomposite formation. Figure 4(b) shows the DTA curve of PTH and CSA-PTHA nanocomposite. The curve shows an endothermic peak at 102 °C, which is the melting point of polythiophene. This peak is shifted to 127 °C for CSA-PTHA nanocomposite which is due to the dehydration effect of the nanocomposite.

Dielectric properties

The dielectric response of the synthesized nanocomposite has been measured as function of the frequency in the range of 1 kHz to 1 MHz. The variation of real (ε'), and imaginary (ε'') part, and ac conductivity (σac) of PTH and CSA-PTHA nanocomposite with the frequency of applied field are shown in figure 5(a). The parameters are calculated using the following relations.

\[
ε' = \frac{C_p d}{ε_o A}
\]

\[
ε'' = ε' \tan δ
\]

\[
σ_{ac} = 2πε''
\]

Where \(C_p\) represents the capacitance measured in pF, \(ε_o\) is the permittivity of free space \((8.854 \times 10^{-12} \text{ F m}^{-1})\), \(A\) represents the cross-sectional area, \(d\) is the thickness of the sample and \(\tan δ\) is the dielectric loss with \(δ\) being phase angle.

The ionic mobility and molecular interaction in polymer nanocomposite was studied using dielectric relaxation. The dissociation of ions in polymer nanocomposite is directly associated to the existence of dipoles. The dielectric relaxation offers information about ion transport property of nanocomposite. Figures 5(a) and (b) shows the variation of dielectric constant and loss with respect to frequency. For all samples, the dielectric constant and loss is found to be decreased with increase in frequency. The dielectric constant arises due to interfacial polarisation in heterogeneous nanocomposite.

The maximum polarisation is obtained at a lower frequency due to which dipoles easily follow the applied electric field, so a high dielectric constant is obtained. Dielectric constant of PTH and PTHA nanocomposites remains almost constant in the higher frequency region, because beyond specific frequency of the applied electric field, molecules do not get enough time to orient themselves in the direction of applied field. The
The dielectric constant was found to be high at lower frequency and it decreases with the increase in frequency, which is considered to be a normal dielectric behavior. The incorporation of Al₂O₃ enhances the dielectric constant of CSA-PTHA nanocomposite. The results indicate that, a higher dielectric constant is obtained for a higher concentration of Al₂O₃, which is attributed to the increase in crystallinity of nanocomposite with the addition of Al₂O₃.

The dielectric constant of CSA-PTHA nanocomposite was found to be more than pure PTH. The dielectric constant of pure PTH is found to be $4 \times 10^2$, whereas that of CSA-PTHA nanocomposite is $1.066 \times 10^3$ at the same applied frequency. There are several reasons for change in dielectric constant such as (i) change in the morphology of polymer nanocomposites due to incorporation of Al₂O₃, (ii) increase in the surface area of polymer nanocomposites which creates large interaction zone and (iii) change in the space charge distribution of CSA-PTHA nanocomposite.

A similar variation is observed for dielectric loss ($\varepsilon''$) is shown in figure 5(b). It is witnessed that the behavior of dielectric loss shows a decreasing trend with an increase in frequency. In low-frequency region, dielectric loss decreases rapidly and in the high frequency region, it decreases slowly. This may be occurring due to the presence of defects and impurities in the nanomaterials.

The temperature dependence of dielectric constant and dielectric loss of PTH and CSA-PTHA nanocomposite are shown in figure 6. The dielectric constant and dielectric loss increases with the temperature and decreases with the frequency. As the temperature increases, the orientation of dipoles and trapped charge carriers arises from total polarisation. Therefore, dielectric constant was increased. The dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) of CSA-PTHA nanocomposite is higher than that of the PTH, for all temperature and frequencies. This is because of the fact that the dielectric permittivity of the material depends on the polarisability of molecules.

**AC conductivity**

The variation of ac conductivity of the PTH and CSA-PTHA nanocomposite with frequency are shown in figure 7.

AC conductivity increases with increase in frequency. It is observed that CSA-PTHA nanocomposite has more AC conductivity compared to PTH. It is also observed that the conductivity gets increased with the incorporation of Al₂O₃ in CSA-PTHA nanocomposite. The total AC conductivity of the dielectric material is the combination of two components which can be expressed by the following equation.

$$\sigma_{ac} = \sigma_{dc} + \sigma(\omega, T)$$

Where $\sigma_{dc}$ is dc conductivity, which arises due to the ionic or electronic conductivity, the second term is frequency dependent ac conductivity which is associated to dielectric relaxation produced by the localised charge carriers. At low frequency region, the frequency independent conductivity is due to dc conductivity, which arises from the orientation of charge carriers over long distance under the applied electric field. As frequency is increased, the mean displacement of charge carrier is reduced thus conductivity is increased due to the activation of trapped charges in the system which undergoes localised motion. It is clear from the figure 5(c) that the conductivity exhibited by CSA-PTHA nanocomposite is higher than that of pure PTH. The conductivity value of pure PTH is found to be $1.89 \times 10^{-4} \text{ S cm}^{-1}$ which is increase with Al₂O₃ concentration, achieving the highest conductivity of $1.209 \times 10^{-3} \text{ S cm}^{-1}$ for CSA-PTHA nanocomposite.
Figure 6. Temperature dependence dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) of PTH (a), (b) and CSA-PTHA nanocomposites (c), (d) respectively.

Figure 7. Temperature dependence ac conductivity of (a) PTH and (b) CSA-PTHA nanocomposite.
Electrochemical studies of PTH and CSA-PTHA modified GCEs

Cyclic voltammetry (CV) experiments were performed in 0.1 M PBS solution in the presence and absence of hydrazine to study the comparative electrocatalytic activity of bare GCE, PTH modified GCE and CSA-PTHA modified GCE. Figure 8(a) shows CVs of bare GCE, PTH modified GCE and CSA-PTHA modified GCE in 0.1 M PBS solution at a scan rate of 50 mVs$^{-1}$ in the absence of hydrazine.

The CV curve of CSA-PTHA nanocomposite modified GCE has larger anodic and cathodic current compared to PTH modified GCE and bare GCE, which clearly indicates that the deposition of CSA-PTHA nanocomposite improves the electrochemical activity of the electrode in PBS buffer solution. The electrolyte containing 0.1 mM hydrazine, bare GCE do not show any significant oxidation peak as shown in figure 8(b). However, PTH and CSA-PTHA nanocomposite modified GCE shows oxidation peak at $\sim$0.99 V ($I_{pa} = 9.31$ $\mu$A) and 0.66 V ($I_{pa} = 1.47$ $\mu$A) respectively. The electrochemical response is irreversible, as no cathodic current is found during reverse sweep. Moreover, the detection potential was observed to be decreasing in the order of CSA-PTHA < PTH < bare GCE. The prominent increase in the anodic peak current of the CSA-PTHA nanocomposite modified GCE suggest a faster electron transfer and thus hydrazine can be detected efficiently through an oxidation reaction process.

The electrochemical impedance spectroscopy (EIS) technique was used to investigate the interfacial properties of the PTH modified GCE and CSA-PTHA modified GCE electrodes. The Nyquist plot measured in a frequency range of 0.1 Hz to 10 kHz and signal amplitude of 10 mV in 0.1 M PBS solution containing 0.1 mM hydrazine is shown in figure 9. The diameter of a semicircle portion at higher frequency region in Nyquist plot corresponds to an electron transfer resistance ($R_{ct}$). In 0.1 M PBS containing 0.1 mM hydrazine, CSA-PTHA modified GCE shows small semicircle at high frequencies and a linear Nyquist plot at low frequencies. Also, the CSA-PTHA modified GCE shows lower interfacial $R_{ct}$ ($94.79$ $\Omega$) than that of the PTH modified GCE ($110.25$ $\Omega$). These facts suggest that the electron transfer is quicker at the CSA-PTHA modified GCE compared with that of PTH modified GCE. The obvious decrease in impedance response of CSA-PTHA modified GCE shows an enhancement in the electrochemical activity, with a higher tendency for the electron transfer process. This may be ascribed due to highly conductive CSA surfactant and nanoparticle that acted as electron transfer channels. Both results of EIS and CV proved that the CSA-PTHA modified GCE has the good electrochemical performance.

Effect of hydrazine concentration on CSA-PTHA modified GCE

To examine the effect of various hydrazine concentrations on the performance of the CSA-PTHA modified GCE electrode, cyclic voltammetry characterisation is performed at 50 mVs$^{-1}$ in 0.1 M PBS solution using different concentrations of hydrazine from 0.25 to 4 mM as shown in figure 10(a). By increasing the hydrazine concentrations from 0.25 mM to 4 mM, a rapid increase in the oxidation peak is observed, which shows the efficient electrocatalytic performance of the modified electrode without any fouling effect. The linear increase in the peak current shows the existence of the active electrocatalytic capability of modified electrode and the enhanced oxidation peak current shows good conductivity and large surface area of CSA-PTHA nanocomposite [33].
These results are clearly demonstrated the outstanding electrocatalytic activity of the CSA-PTHA modified GCE towards the oxidation of hydrazine through direct electron transfer behavior. The oxidation reaction of hydrazine can be represented by the following equation:

$$\text{N}_2\text{H}_4 + 4\text{H}_2\text{O} \rightarrow \text{N}_2 + 4\text{H}_3\text{O}^+ + 4e^-$$

The calibration curve made from the above CV curve is presented in Figure 10(c). The plot of oxidation peak current versus hydrazine concentration is observed to be linear with correlation coefficient ($R^2 = 0.9994$), suggesting that the electrocatalytic reaction follows first-order kinetics with respect to hydrazine concentration.

**Effect of scan rate on the CSA-PTHA modified GCE**

The kinetics of hydrazine oxidation on CSA-PTHA modified GCE was also studied by examining the effect of varying the scan rate on the voltammetry response. Figure 10(b) shows the effect of scan rate in the presence of 1 mM hydrazine on the CSA-PTHA modified GCE. The CV curves were recorded in 0.1 M PBS containing 1 mM hydrazine at various scan rates from 20 to 100 mVs$^{-1}$. A well-defined oxidation peak current of hydrazine increased linearly with the increase of scan rate from 20 to 100 mVs$^{-1}$. Figure 10(d) shows the plot of oxidation peak current versus the square root of scan rate. It presents a linear relationship, therefore the electrocatalytic oxidation of hydrazine on CSA-PTHA modified GCE is an electrochemically irreversible process [34]. The linear regression equation can be expressed as $y = 48.2101 + 11.2101x$ with correlation coefficient $R^2 = 0.99128$. It is observed that hydrazine oxidation peak current is proportional to the square root of scan rate which is shows that the oxidation of hydrazine on the CSA-PTHA modified GCE is a diffusion controlled process [35].

**Amperometric detection of hydrazine at PTH and CSA-PTHA modified GCEs**

The amperometric method based on measurement of $i$-$t$ response at a fixed potential would lead to high precision and more consistent data than other voltammetric techniques.

Figures 11(a) and (b) shows the typical amperometric response of PTH and CSA-PTHA modified GCE with continuous addition of 10–35 μM and 10–90 μM hydrazine respectively into 0.1 M PBS at applied potential of 0.5 V under constant stirring. After the successive addition of hydrazine, the amperometric sensor shows a fast increase in the oxidation current, indicating that the sensor has fast response. For each sample injection, the subsequent hydrazine oxidation current reached its maximum value, which implies a rapid response towards hydrazine detection. At first, we used hydrazine concentrations from 10–35 μM with 5 μM difference for each interval for CSA-PTHA modified GCE. In order to see the effect of sudden increase in the concentration of hydrazine on the CSA-PTHA modified GCE, we dropped 15 μM hydrazine in the next step. It leads to sudden increase in the current from 120 μA to 165 μA from 35 μM to 50 μM concentration. This confirms that the amperometric sensor shows fast increase in the oxidation current, indicating the fast response of the sensor. This
phenomenon comes from the fact that CSA-PTHA nanocomposite has low resistance and high electron transfer rate, which significantly reduces the current response time.

Additionally, the amperometric current was observed to be linearly correlated with the hydrazine concentration for both PTH modified GCE and CSA-PTHA modified GCE. Figures 1(a) and (b) shows the calibration curve achieved for the oxidation current versus hydrazine concentration. The correlation coefficient of the line $R^2 = 0.99924$ and the linear equation is $y = 0.7127 + 0.0196x$ for PTH modified GCE, whereas $R^2 = 0.99668$ and linear equation is $y = 71.7918 + 1.51542 \times$ for CSA-PTHA modified GCE. The sensitivities of the modified electrodes were found to be $0.2854 \mu A \mu M^{-1}cm^{-2}$ for CSA-PTHA modified GCE and PTH modified GCE, respectively. The limit of detection (LOD) of the modified electrode is calculated using following equation

$$\text{LOD} = \frac{3 \times S_d}{m}$$

Where $m$ represents the slope of the calibration plot and $S_d$ is the standard deviation and it is found out to be $12.652$ and $0.11 \mu M$ for PTH modified GCE and CSA-PTHA modified GCE respectively at a signal to noise ratio of 3.

Comparing the results, it is found that the CSA-PTHA modified GCE shows much higher sensitivity and low detection limit than those by PTH modified GCE. The important analytical parameters such as linear range, sensitivity and detection limit of CSA-PTHA modified GCE were compared with the other functional materials modified electrode for hydrazine sensors listed in the table 1. It can be identified from this comparison table that CSA-PTHA modified GCE electrode shows very low hydrazine detection limit. Thus, CSA-PTHA modified GCE is an appropriate electrode material for sensitive hydrazine detection.
Conclusions

In summary, newly developed and effective hydrazine electrochemical sensor is fabricated using PTH and CSA-PTHA nanocomposite prepared using in situ chemical oxidative polymerisation method. The prepared nanocomposites was characterised using XPS, AFM, DSC/DTA and impedance analysis. The dielectric measurement confirms that the synthesised CSA-PTHA nanocomposite combines the dielectric properties of Al₄O₃ and the electrical properties of polythiophene. A cyclic voltammetry study reveals CSA-PTHA modified GCE based electrochemical sensor exhibits good electrocatalytic effect for hydrazine oxidation compared to

Table 1. Applied potential, linear range, limit of detection and sensitivity of different electrochemical hydrazine sensors from literature.

| Material                  | Potential (V) | Linear range (μM) | Detection limit (μM) | Sensitivity (μA/μM⋅cm⁻²) | References |
|---------------------------|---------------|-------------------|----------------------|-------------------------|------------|
| PEDOT-Cu₂O               | 0.4           | 0.5–600           | 0.2                  | 0.414                   | [36]       |
| PTh-ZnO                  | 0.55          | 0.5–48            | 0.207                | 1.22                    | [21]       |
| ZnO/MWCNT/GCE            | 0.4           | 0.6–250           | 0.18                 | 0.247                   | [37]       |
| α–Fe₂O₃/CPANI            | 0.3           | 0.2–40            | 0.153                | 1.93                    | [38]       |
| CuS-rGO                  | 0.3           | 1–1000            | 0.3                  | 0.008                   | [39]       |
| PANI-ZnCo₂O₄             | 0.55          | 600–1050          | 0.2                  | 0.43                    | [40]       |
| Fe₃O₄/Ppy/GO             | 0.2           | 0.005–1.275       | 1.4                  | 0.44                    | [41]       |
| CSA-PTHA                 | 0.5           | 10–90             | 0.18                 | 0.285                   | This work  |

Figure 11. (a) and (b) amperometric response i–t curve of the PTH modified GCE and CSA-PTHA modified GCE respectively during successive addition of hydrazine in 0.1 M PBS solution at fixed potential of 0.5 V (c) & (d) Calibration plot of the current versus hydrazine concentration.

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| CuS-rGO                  | 0.3           | 1–1000            | 0.3                  | 0.008                   | [39]       |
| PANI-ZnCo₂O₄             | 0.55          | 600–1050          | 0.2                  | 0.43                    | [40]       |
| Fe₃O₄/Ppy/GO             | 0.2           | 0.005–1.275       | 1.4                  | 0.44                    | [41]       |
| CSA-PTHA                 | 0.5           | 10–90             | 0.18                 | 0.285                   | This work  |
PTH. The current amperometric sensor developed from CSA-PTHA modified GCE shows low LOD of 0.18 \( \mu M \) and a high sensitivity of 0.285 \( \mu A \mu M cm^{-2} \) in a wide linear range of 10–90 \( \mu M \) hydrazine. Our results reveal that the combination of conducting polymer with metal oxide could provide an efficient way to fabricate advanced and economical electrochemical sensors.

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**References**

[1] Cui L et al 2014 Unique tri-output optical probe for specific and ultrasensitive detection of hydrazine Anal. Chem. 86 4611–7
[2] Benvidi A, Kakolaki F, Zare H R and Vafazadeh R 2011 Electrocatatotic oxidation of hydrazine at a Co (II) complex multi-wall carbon nanotube modified carbon paste electrode Electrochim. Acta 56 2045–50
[3] Yin W X, Li Z P, Zhu J K and Qin H Y 2008 Effects of NaOH addition on performance of the direct hydrazine fuel cell J. Power Sources 182 520–3
[4] Ameen S, Akhtar M S and Shin H S 2012 Hydrazine chemical sensing by modified electrode based on in situ electrochemically synthesized polyaniline/graphene composite thin film Sens. Actuator B-Chem. 173 177–83
[5] Ho T D, Yeh P M, Chetwyn N P, Wang J, Anderson J L and Zhong Q 2014 Determination of trace level genotoxic impurities in small molecule drug substances using conventional headspace gas chromatography with contemporary ionic liquid dilluents and electron capture detection J. Chromatogr. A 1361 217–28
[6] Gionfriddo E, Naccaraato A, Sindona G and Tagarelli A 2014 Determination of hydrazine in drinking water: development and multivariate optimization of a rapid and simple phase microextraction-gas chromatography-triple quadrupole mass spectrometry protocol Anal. Chim. Acta 835 37–47
[7] Safavi A and Karimi M A 2002 Flow injection chemiluminescence determination of hydrazine by oxidation with chlorinated isocyanurates Talanta 58 785–92
[8] Karuppiyah C, Palanisamy S, Chen S M, Ramaraj S K and Perikaruppan P 2014 A novel and sensitive amperometric hydrazine sensor based on gold nanoparticles decorated graphite nanosheets modified screen printed carbon electrode Electrochim. Acta 139 157–64
[9] Azad U P and Ganesan V 2011 Determination of hydrazine by polyNi (II) complex modified electrodes with a wide linear calibration range Electrochim. Acta 56 5766–70
[10] Liu Y, Li B B, Wei W, Wan Q J and Yang N J 2013 A simple and high-performance hydrazine sensor based on graphene nano platelets supported metal nanoparticles Adv. Mater. Res. 794 246–51
[11] Numan A, Shahid M M, Omar F S, Ramesh K and Ramesh S 2017 Facile fabrication of cobalt oxide nanograin-decorated reduced graphene oxide composite as ultrasensitive platform for dopamine detection Sens. Actuator B-Chem. 238 1043–51
[12] Shukla S, Chaudhary S, Umar A, Chaudhary G R and Mehta S K 2014 Tungsten oxide (WO3) nanoparticles as scaffold for the fabrication of hydrazine chemical sensor Sens. Actuator B-Chem. 196 231–7
[13] Le I, Lu X, Wang W, Bian X, Xue Y, Wang C and Li L 2012 Fabrication of MnO2/graphene oxide composite nanosheets and their application in hydrazine detection RSC Adv. 2 2541–4
[14] Khan S B, Faisal M, Rahman M M, Abdel-Latif I A, Ismail A A, Akhtar K, Al-Hajry A, Abdullah M A and Alamry K A 2013 Highly sensitive and stable phenyl hydrazine chemical sensors based on CuO flower shapes and hollow spheroid New J. Chem. 37 1098–104
[15] Zhang J, Gao W, Dou M, Wang F, Liu J, Li Z and Ji H 2015 Nanorod-constructed porous Co3O4 nanowires: highly sensitive sensors for the detection of hydrazine Analyst 140 1686–92
[16] Tripathi A, Misra K P and Shukla R K 2013 Enhancement in ammonia sensitivity with fast response by doping Al2O3 in polyaniline J. Appl. Polym. Sci. 130 1941–8
[17] Xu F, Liu Y, Ding G, Deng M, Chen S and Wang L 2014 Three dimensional macroporous poly (3, 4-ethylenedioxythiophene) structure: electrodeposition preparation and sensor application Electrochim. Acta 150 223–31
[18] Kong F, Wang Z, Zhang J, Xia H, Zhu B, Wang Y, Wang S and Wu S 2008 The preparation and gas sensitivity study of polythiophene/SnO2 composites Mater. Sci. Eng. B 150 6–11
[19] Harraz F A 2014 Electrochemical formation of a novel porous silicon/polypyrrole hybrid structure with enhanced electrical and optical characteristics J. Electroanal. Chem. 729 68–74
[20] Skompska M 2010 Hybrid conjugated polymer/semiconductor photovoltaic cells Synth. Met. 160 1–15
[21] Faisal M, Harraz F A, Al-Salami A E, Al-Sayari S A, Al-Hajry A and Al-Asiri M S 2018 Polythiophene/ZnO nanocomposite-modified glassy carbon electrode as efficient electrochemical hydrazine sensor Mater. Chem. Phys. 214 26–34
[22] Feng W, Wan A S and Garfunkel E 2013 Interfacial bonding and morphological control of electropolymerized polythiophene films on ZnO J. Phys. Chem. C 117 9852–63
[23] Dakshayini B S, Reddy K R, Mishra A, Shettip N P, Basu S, Naveen S and Raghu N V 2019 Role of conducting polymer and metal oxide-based hybrids for applications in amperometric sensors and biosensors Microchim. Acta 177 1–24
[24] Ramkumar R and Sangaranarayanan M V 2019 Electrochemical sensing of anesthetics using polythiophene coated glassy carbon electrodes Chemistry Select 4 9776–83
25. Inagaki C S, Oliveira M M, Bergamini M F, Marcolino-Junior L H and Zarbin A J 2019 Facile synthesis and dopamine sensing application of three component nanocomposite thin films based on polythiophene, gold nanoparticles and carbon nanotubes J. Electroanal. Chem. 840 208–17

26. Ramachandran T and Dhayabaran V V 2019 Utilization of a MnO2/polythiophene/rGO nanocomposite modified glassy carbon electrode as an electrochemical sensor for methyl parathion J Mater Sci-Mater El 30 12315–27

27. Vijeth H, Ashokkumar S P, Yesappa L, Niranjana, Vandana M and Devendra Rappa H 2019 Camphor sulfonic acid assisted synthesis of polythiophene composite for high energy density all-solid-state symmetric supercapacitor J. Mater. Sci., Mater. Electron. 1–14

28. Heeg J, Kramer C, Wolter M, Michaelis S, Plieth W and Fischer W J 2001 Polythiophene-O3 surface reactions studied by XPS Appl. Surf. Sci. 180 36–41

29. Meguedad A and Benharrats N 2012 Thermal degradation behavior of polythiophene-modified montmorillonite nanocomposite J. Anal. Sci. Technol. 3 193–201

30. Kadac K and Nowaczyk J 2016 Polythiophene nanoparticles in aqueous media J. Appl. Polym. Sci. 133 43495–56

31. Maiti S, Shrivastava N K, Suin S and Khatua B B A 2013 strategy for achieving low percolation and high electrical conductivity in melt blended polycarbonate (PC)/multiwall carbon nanotube (MWCNT) nanocomposites: Electrical and thermo-mechanical properties Expr Polym Lett. 7 505–18

32. Tewari D C, Sen V and Sharma R 2012 Temperature dependent studies of electric and dielectric properties of polythiophene based nano nanocomposite Indian J. Pure Appl. Phys. 50 49–56

33. Harraz F A, Ismail A A, Al-Sayari S A, Al-Hajry A and Al-Assiri M S 2016 Highly sensitive amperometric hydrazine sensor based on novel α-Fe2O3/crosslinked polyaniline nanocomposite modified glassy carbon electrode Sens. Actuator B-Chem. 234 573–82

34. Streeter I, Wildgoose G G, Shao L and Compton R G 2008 Cyclic voltammetry on electrode surfaces covered with porous layers: an analysis of electron transfer kinetics at single-walled carbon nanotube modified electrodes Sens. Actuator B-Chem. 133 462–6

35. Sakthivel M, Ramaraj S, Chen S M, Dinesh B and Chen K H 2018 A highly conducting flower like Au nanoparticles interconnected functionalized CNFs and its enhanced electrocatalytic activity towards hydrazine through direct electron transfer J. Taiwan Inst. Chem. Eng. 82 64–74

36. Xu F, Liu Y, Xie S and Wang L 2016 Electrochemical preparation of a three dimensional PEDOT–Cu2O hybrid for enhanced oxidation and sensitive detection of hydrazine Anal. Methods 8 316–25

37. Fang B, Zhang C, Zhang W and Wang G 2009 A novel hydrazine electrochemical sensor based on a carbon nanotube-wired ZnO nanoflower-modified electrode Electrochim. Acta 55 178–82

38. Harraz F A, Ismail A A, Al-Sayari S A, Al-Hajry A and Al-Assiri M S 2016 Highly sensitive amperometric hydrazine sensor based on novel α-Fe2O3/crosslinked polyaniline nanocomposite modified glassy carbon electrode Sens. Actuator B-Chem. 234 573–82

39. Yang Y J, Li W and Wu X 2014 Copper sulfide reduced graphene oxide nanocomposite for detection of hydrazine and hydrogen peroxide at low potential in neutral medium Electrochim. Acta 123 260–7

40. Omar F S, Numan A, Duraisamy N, Bashir S, Ramesh K and Ramesh S 2017 A promising binary nanocomposite of zinc cobaltite intercalated with polyaniline for supercapacitor and hydrazine sensor J. Alloys Compd. 716 96–105

41. Yang Z, Sheng Q, Zhang S, Zheng X and Zheng J 2017 One-pot synthesis of Fe3O4/polyppyrrrole/graphene oxide nanocomposites for electrochemical sensing of hydrazine Microchim. Acta 184 2219–26