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Synthesis, Characterization of Green Tea Stabilized Iron Nanoparticles and their Synergistic Effect on Polyaniline

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Abstract

This work reports the synthesis of polydisperse iron nanoparticles (FeNPs) stabilized on green tea polyphenol stabilizing and capping agents. An in-built template synthesis method was employed which requires no post-synthesis template removal. The green tea extracts at temperatures 25, 50, 75, 90 °C were used. The characteristics of the 'green synthesis' processed FeNPs were evaluated through UV-Vis spectroscopy, High Resolution Tunneling Microscopy (HRTEM), Electrochemical Impedance Spectroscopy (IES) and Cyclic Voltammetry (CV). UV-Vis results indicated formation of the FeNPs peaks at 280 and 350 nm as the HRTEM results showed that the FeNPs were spherical and polydisperse with diameter ranges 50-200nm. The FeNPs were embedded (HRTEM results) onto the polyols which indicated their stabilizing and capping roles. Energy Dispersive X-ray Spectroscopy (EDX) revealed the FeNPs majorly constituted of Iron. Electrochemical Impedance Spectroscopy (EIS) results indicated that the charge transfer resistance (R_{ct}) of Pt-FeNPs modified electrode was lower ($R_{ct} = 1.8905 \times 10^6 \Omega$) compared to that of the bare Pt electrode ($1.0982 \times 10^7 \Omega$) indicating that the synthesized FeNPs have good conductivity. Analysis of the cyclic voltammograms for the Pt/ FeNPs and Pt/PANi (polyaniline) led to the calculation of the corresponding kinetic parameters.

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Electrode modification during electrochemical studies was done via a simple drop-coating-then- drying technique. The diffusion coefficient (D_e , cm^2/s) and heterogeneous rate constants (k^0 , cm/s) calculated for the FeNPs were 1.44×10^{-5} and 0.028 respectively. Those for the PANi/Pt system were found to be 3.25×10^{-7} and 9.52×10^{-4} which were characteristic of an electron hopping process along a polymer chain. It means slower electron transfer kinetics on the PANi system than on the FeNPs system. On composing the PANi/FeNPs hybrid, the new D_e and k^0 values obtained were 8.76×10^{-6} and 9.64×10^{-3} respectively. There was an enormous 3-fold, 27 times, 10-fold increase in the current, diffusion coefficient and heterogeneous rate constant respectively of the FeNPs/PANi/Pt composite compared to that of unmodified PANi. It means the FeNPs can greatly improve (synergistic effect) the electromediation properties of PANi.

Keywords: Green tea extract; Iron nanoparticles; Polyaniline; Synergistic effect; Diffusion coefficient; heterogeneous rate constant

1. Introduction

For over several decades now, a lot of research interest has continued to focus on polyaniline (PANi) [1-3]. Polyaniline exhibits a host of excellent characteristics such as good electrical conductivity, good environmental stability as well as a facile synthetic process [4-6] which has seen it applied in several areas. To this effect, PANi based biosensors, actuators; electrical diodes have been reported [7-9]. Recently it has been discovered that nano-sized PANi/metal composites/hybrids exhibit even better characteristics as compared to the lone polymer [10]. Several methods including chemical and electrochemical oxidative methods, in-situ reverse microemulsion, and one-pot synthesis techniques have been used to prepare such conducting polymer/metal nanocomposites [10].

Here we report the synthesis of nanopolyaniline iron nanoparticle hybrids via a simple drop-coating- then-drying technique onto pre-prepared PANi/Pt electrodes. The aim was to verify whether, despite the simplicity of the composite preparation method, such composites still possess good synergistic properties just like those from other methods.

The iron-nanoparticles are first synthesized through the reduction of the ferric chloride salt with green tea herbal extracts. Green tea is a king plant in the medicinal plant kingdom owing to its high antioxidant effect in scavenging for free radicals in the body [11]. However, its utility as a nanoparticle fabrication precursor has not been reported yet and/or scarce. Its high antioxidant properties are due to the fact that it contains large quantities of polyphenols. It is believed that this polyols can also play a key role as stabilizers/capping agents in the production of the iron nanoparticles [12]. In particular, the high content of (-)-epicatechin, (-)-epicatechingallate, (+)-gallocatechin amongst other flavanoids [13] makes it suitable for this role. The novelty of this work firstly, lies on the fact that the green tea FeNPs synthetic process has not been reported. Secondly, the synergistic effect of loading PANi with green synthesized FeNPs has not been demonstrated. Cyclic voltammetry (CV), ultraviolet-visible

spectroscopy (Uv-Vis), electrochemical impedance spectroscopy (EIS), high resolution tunneling electron

microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDX) were used for the characterization process.

2. Materials and Methods

2.1 Materials and chemicals

The iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, >98%) was from Fluka. Green tea was bought from a local supermarket (Tusky's, Kenya). Distilled deionised water (DDW) was from the analytical laboratory, Chemistry Department, University of Nairobi and was used for all aqueous preparations. All the chemicals were used as received.

2.2 Extraction process and FeNPs synthesis

Exactly 10g of green tea was weighed and placed into 100mL DDW with vigorous stirring for 30 min. The resultant mixture was then centrifuged at 8000 revolutions per minute (rpm) for another 30 min. The resultant supernatant was collected, filtered and stored at -20°C before use.

The FeNPs were prepared by adding 0.1 M iron III chloride solution to the green tea extract (supernatant at ambient temperature) in a 2:1 volume ratio. The mixture was hand shaken for 1 min and allowed to stand at room temperature for 1 hr. In a nutshell, 4 mL of 0.1 M FeCl_3 solution were added to 2mL of the green tea extracts at 25, 50, 75 & 90°C to prepare the nanoparticles.

2.3 Instrumental characterization of the FeNPs

The Uv-Vis studies of the FeNPs, the green tea extracts and the Fe^{3+} solution were studied on a Nicolet Evolution 100 (Thermo Electron Cooperation, UK). The samples were diluted ten times before the study. Quartz cuvettes were used and a wavelength range of 250-700 nm maintained.

A Tecnai G²F20 X-Twin MAT (US) instrument operating at 200kV was used for all the HRTEM studies. A drop of the samples (dispersed in DDW water) was placed over the carbon-coated standard copper grids and allowed to dry prior to measurements. The instruments were equipped with an energy dispersive X-ray (EDX) detector (Oxford LINK_ISIS 300) for elemental composition analysis and the EDX spectra were measured at an accelerating voltage of 10 kV. The FeNPs samples were randomly selected for analysis.

2.4 Electrochemical studies

2.4.1 Electrochemical impedance spectroscopy

Electrochemical impedance spectra (EIS) measurements were performed using Volta Lab PGL 402 from Radiometer Analytical (Lyon, France) in a solution containing 1 M Hal and plotted in the form of complex plane diagrams (Nyquist plots) with a frequency range of 100 kHz to 0.1 Hz. The amplitude of the applied sine wave potential was 10 mV, where as the ambient Dc potential was set at a formal potential of 184 mV. The experiment was run for the bare electrode and then with an electrode drop coated with the synthesized FeNPs to

study the conducting and catalytic properties of the FeNPs.

2.4.2 Cyclic voltammetry

All the electrochemical experiments were carried using a BAS100W integrated and automated electrochemical work station from Bioanalytical systems (BAS), Lafayette, USA. The cyclic voltammograms were recorded with a computer interfaced to the BAS 100W electrochemical work station.

A 3 mL electrochemical cell with a conventional three electrode configuration was used. The three electrodes were: (1) a platinum working electrode (Pt), (2) A 0.5 mm diameter platinum auxiliary electrode from sigma Aldrich, South Africa and (3) Ag/AgCl/3M NaCl reference electrode. Both the working and the reference electrodes were from BAS. Proper electrode hygiene was maintained during all electrochemical measurements by thorough sequential polishing of the working electrode onto various size alumina slurries and thorough rinsing with DDW after each polishing stage. The Platinum counter electrode was occasional flamed cleaned to remove any adhered impurities.

2.4.3 Electrochemical Characterization of the FeNPs, electrodeposition of polyaniline

A small amount of the synthesized iron nanoparticles (FeNPs) were dropped on to the 0.177 cm² are platinum working electrode. Electro-characterization was done in 1 M HCl supporting electrolyte at potential window of -100-1000mV at different scan rates.

The electrodeposition of PANi onto the platinum working electrode under the cyclic voltammetric mode was done at the same potential window as above. Electrodeposition took place at a scan rate of 100 mV/s. Hydrochloric acid (1M) was the supporting electrolyte and the concentration of the aniline monomer.

2.4.4 Electrochemical Characterization of the FeNPs/PANi hybrids

The FeNPs/PANi hybrids were prepared by drop-coating a 2 μ L dispersion of the FeNPs in hexane onto the platinum working electrode followed by drying in the open air. Care was taken to drop-coat only the 0.0177cm² active electrode surface area was coated. Any other extraneous coating was scrapped off. The potential window for characterization was maintained constant as above for easy comparison. Scan rates of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mV/s in 1M supporting electrolyte was done in order to evaluate the electrochemistry of the FeNPs/PANi hybrids coated on the platinum working electrode.

3. Results

3.1 UV-Visible results of the green tea extracts, FeNPs and the ferric chloride solution

Figure 1 (a) the below is a UV-Vis spectrum of the green tea extract at an extraction temperature of 50°C. The spectrum shows a prominent peak at absorption maxima of 272 nm which has been assigned to the $\pi \rightarrow \pi^*$ transitions of the green tea polyols. The high absorbance value of 1.5 obtained indicates a high concentration of

the polyols in solution. Figure 1(b) is the corresponding spectrum for a 10 mM solution of ferric chloride in water. A broad peak extending from 260-380 nm with absorption maxima at 298 nm was seen. Such observation is characteristic of transition metal elements where the observed broad peaks are due to transitions within the filled and unfilled d-orbitals compounded by influence from other external factors.

On addition of the ferric chloride solution to the green tea extracts in a volume ratio 2:1, the spectrum labeled c in figure 1 was recorded. There was a complete disappearance of the Fe^{3+} peak at 298 nm meaning probably a new chemistry is involved. The new peak formed was slightly shifted bathochromically compared to the 272 nm peak of the green tea extracts. This peak at 280 nm and the smaller hub at around 350 nm have been shown to be due to the presence of the iron nanoparticles in the Fe^0 state [14]. It means the reductant polyols within the green tea matrices successfully reduced the iron III ions to the iron zero states also indicating the formation of the FeNPs/polyols hybrid. The reduction of the prominent extract peak at 272 nm indicates the polyols were actually involved in the reduction process and the consequent formation of a new compound (the FeNPs/PANi composite). The actual integration and the nanostructurization effect of the green tea polyphenols/flavanoids were actually evident in the HRTEM images obtained (see below).

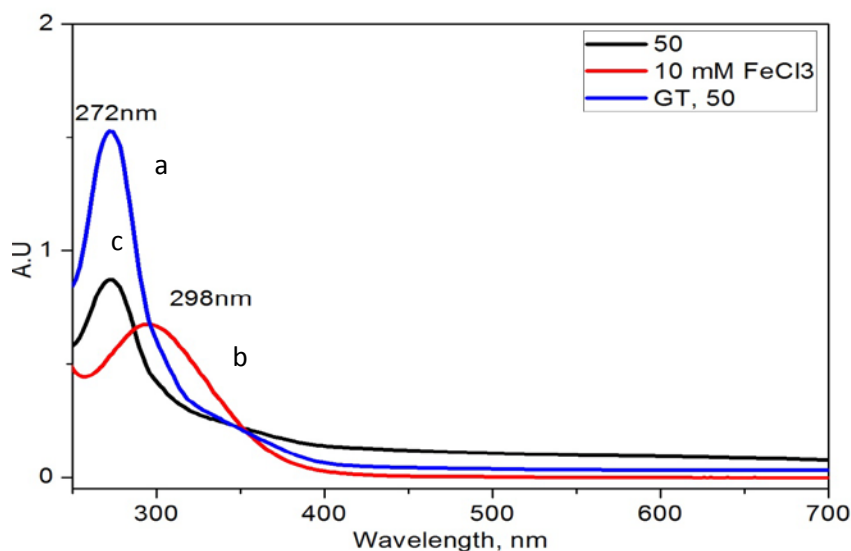


Fig. 1: UV-Visible spectrum for green tea extracts at 50°C (a), FeCl_3 solution (b) and the synthesized FeNPs (c)

3.2 High resolution tunneling electron microscopy

Figure 2 (a) is the HRTEM of the synthesized iron nanoparticles. The micrographs show the FeNPs are spherical in nature with diameter sizes of 50-200 nm and occurred embedded within the polyphenol matrices mostly as solitary particles (Figure 2 inset). The polyols appear as 'white' aggregates in the HRTEM micrographs due to the charging effects emanating from their insulating characters. It means the green tea polyols act as reductant stabilizers for the FeNPs. Similarly capped FeNPs have been reported using sorghum extracts as the reducing agents [15]. Figure 2 (b) gives the EDX results for the FeNPs. The particles are primarily composed of iron which exhibited peaks at 0.4, 0.5, 0.6, 6.5 and 7.0 keV. The elemental analysis of the FeNPs gave atomic compositions of 37.88 C, 17.64 O, 16.01 Fe, and 28.45 Cu indicating the successful

synthesis of the iron nanoparticles. The presence of Cu peaks as seen in the EDX results has been attributed to the copper grid used during the HRTEM analysis.

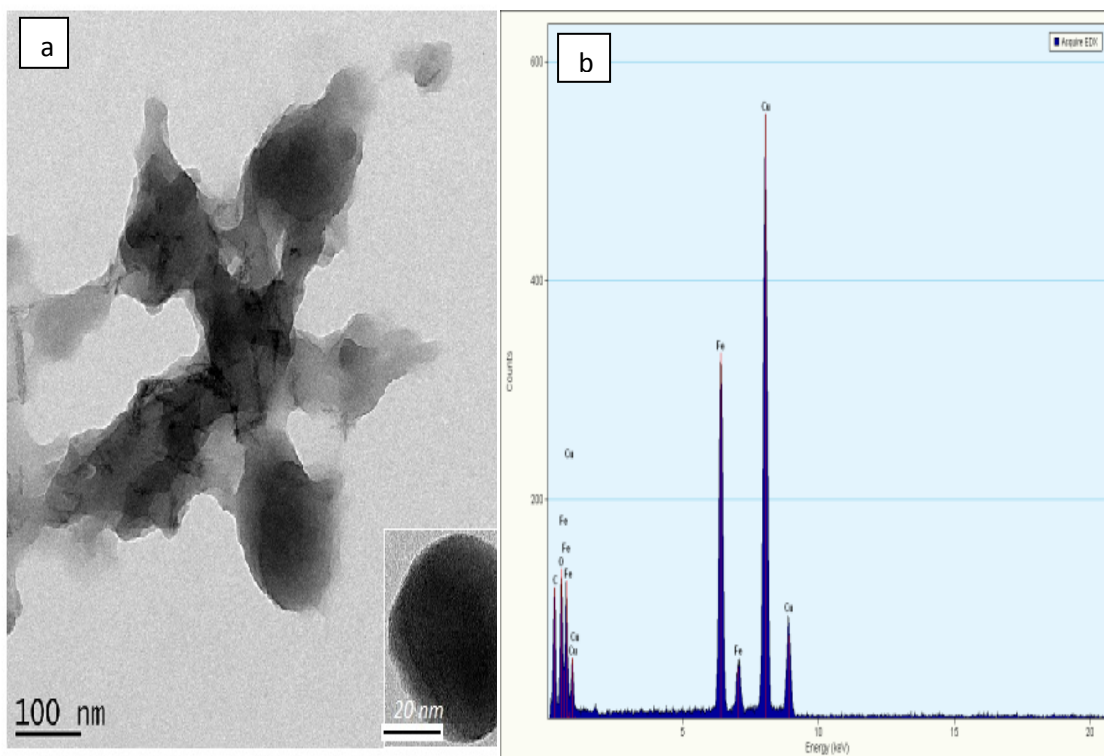


Fig. 2: HRTEM micrographs showing formation of FeNPs within the green tea matrices (a). EDX spectra of the FeNPs showing they are composed of iron (b).

3.3 Electrochemical behavior of the FeNPs

A cyclic voltammetric experiment at a -100 to 1000mV potential window and scan rate of 60 mV/ s gave rise to a reversible redox couple for the FeNPs at a formal potential (E^0) of 425 mV versus the Ag/AgCl, 3M NaCl reference electrode (figure 3, a). The cathodic to anodic peak-to-peak separation was 70 mV. The ratio of the cathodic peak current I_{pc} to that of anodic peak current I_{pa} was close to unity for all the scan rates indicating the FeNPs exhibited reversible electrode kinetics with a fast rate of electron shuttling across the solution electrode interface. On continuous cycling the potential of the FeNPs/Pt electrode in 1 M HCl solution at various scan rates, similar redox wave forms were recorded (figure 3, b). It means the FeNPs were stable at all scan rates in acidic media.

Figure 4 (a) below is a plot of the anodic peak current versus square root of scan rate. A non-zero slope (b1) of 1.66×10^{-5} is characteristic of a diffusion controlled process. Similarly the plot of the cathodic peak current versus scan rate (Fig. 4, b) gave a non-zero intercept and a slope of 3.36×10^{-5} . The value agrees well with the behavior of a thin film adsorbed on the surface of the electrode undergoing a Nernstian reaction [17]. A plot of log peak current against log scan rate gave a slope of 0.6596 which is an intermediate value between 0.5 and 1. This is an indication of both diffusion and adsorption electrochemistry

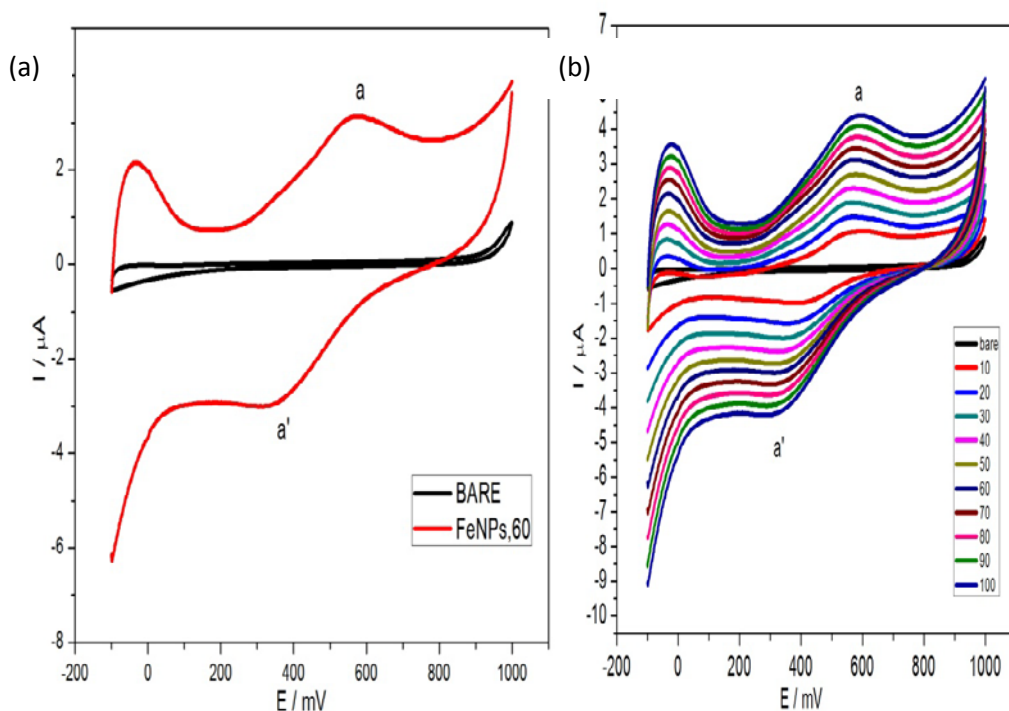


Fig. 3: Reversibility of the FeNPs in 1M HCl on platinum at 60 mV/s (a). A multi-scan rate voltammogram of FeNPs in the same solutions showing the stability of the redox couple (b)

It was of interest to evaluate both the diffusion coefficient (D_e , cm^2/s) and the heterogeneous rate constant (k^0 , cm/s) in order to understand the role of the FeNPs in facilitating electron movement between the platinum electrode and the supporting electrolyte interface. For a reversible couple undergoing Nernstian behavior, the rate of electron diffusion across the electrode/solution interface can be estimated on the equation [18];

$$I_p = 2.69 \times 10^5 n^{3/2} A C_o^* D_e^{1/2} \nu^{1/2} \quad (1)$$

Where : n is the number of electrons transferred; I_p is the peak current in Amperes, A is the electrode area (cm^2); C_o^* is the bulk concentration ($\text{mol}/\text{cm}^{-3}$); D_e is the diffusion coefficient (cm^2/s) and ν is the scan rate in volts/second.

In this case the $\text{Fe}^{3+}/\text{Fe}^0$ reduction was a three electron process. During the evaluation of the diffusion coefficient value, the FeNPs bulk concentration, C_o^* , was replaced by the surface concentration, Γ^* (mol/cm^2). This is in order since the FeNPs were immobilized onto the platinum working electrode and not in solution. From the $2\mu\text{L}$ FeNPs dispersion drop-coated on the electrode, a surface concentration of $1.78 \times 10^{-7} \text{ mol}/\text{cm}^2$ was worked out. Based on equation (1) and the Γ^* value, a diffusion coefficient value of 1.44×10^{-5} was calculated for the FeNPs/Pt system. This indicates the rate of electrode shuttling is moderately fast.

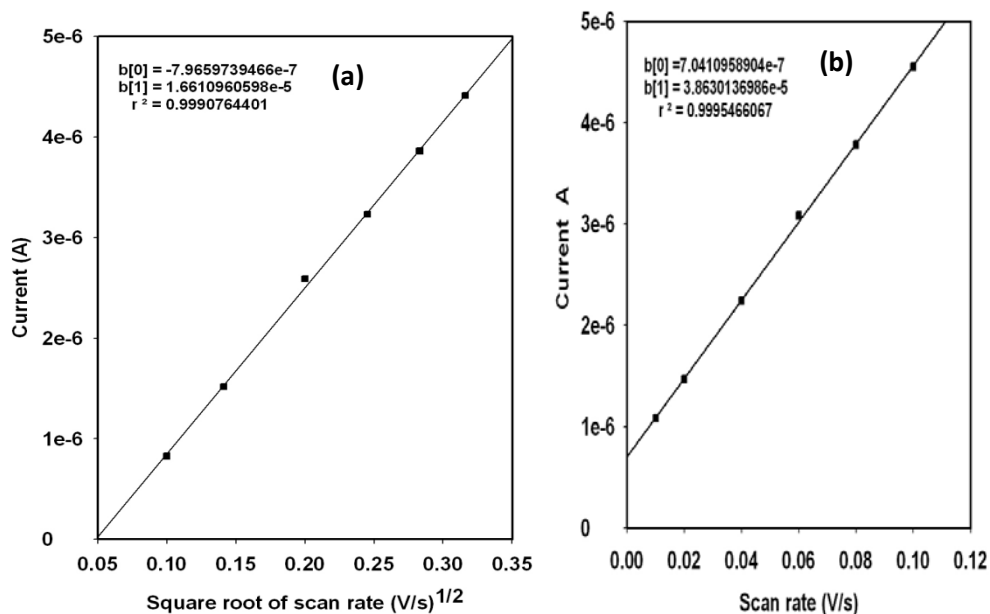


Fig. 4: Plot of anodic peak current versus square root of scan rate (V/s)^{1/2} (a) and the corresponding plot of cathodic peak current versus scan rate (V/s) (b)

The heterogeneous rate constant k^0 (cm/s) is a measure of the kinetic facility of a redox process [19]. Small values to the tune of 10^{-12} indicate a large energy barrier for the forward reaction meaning such a reaction only occurs to a small extent. Large heterogeneous rate constant values on the other hand depict otherwise. Normally ionic and /or metallic species should have a heterogeneous rate constant of about 10 cm/s [19]. However, the encapsulation of the FeNPs within the insulating nanostructuring polyols led the system to slightly tend towards quasi-reversibility. In order to cater for this, the heterogeneous rate constant were estimated based on the Nicholson and Shain equation [19];

$$k^0 = \Psi \left[\frac{\pi D_e n F v}{RT} \right]^{1/2} \quad (2)$$

Where: Ψ is a parameter dependent on the peak to peak separation of a redox couple. The k^0 (cm/s) value of 0.028 cm/s obtained, though lower than that of the ionic/metallic conductors, indicate fairly fast electrode exchange process.

3.4 Electrochemical impedance (IES) characterization of the FeNPs

The resistance to charge transfer of the synthesized iron nanoparticles was monitored using EIS method which is effective in probing the features of the surface modified electrodes. The Nyquist plot of the impedance spectra comprises a semicircle portion and a linear portion. The semicircle portion (occurs at high frequencies) of this plot is applied to explain the electron transfer process. Using the charge transfer resistance (R_{ct}) at the electrode which is equal to the semicircle diameter, one can describe the electrode interface properties. Figure 5 below

show the semicircle plot obtained on subjecting the FeNPs modified platinum electrode to analysis. Similar experiment was done with an unmodified (bare) electrode for comparison. Inset is the equivalent circuit fitted in order to obtain the impedance parameters.

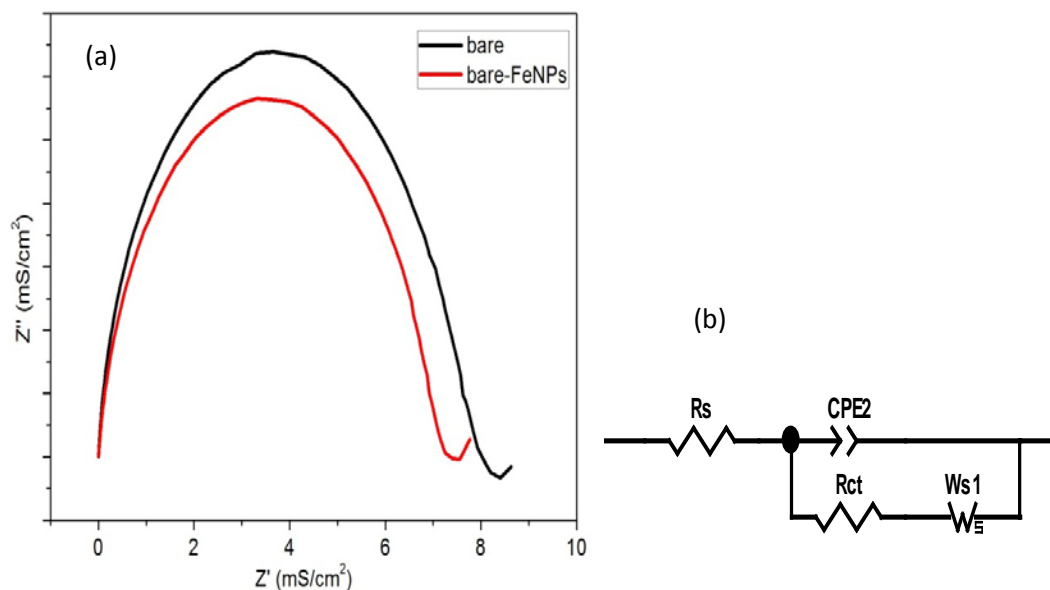


Fig. 5: The Nyquist plot of the FeNPs on a platinum electrode (a) and on a bare electrode (b) and the equivalent circuit used for fitting

In the circuit, R_s is the solution resistance, R_{ct} is the charge transfer resistance and CPE (constant phase element) is a distributive element that models the double layer capacitance owing to the surface in homogeneity while Z_w (W_s) measures mass transport (mass transport impedance). The impedance parameters obtained are collected in table 1 below. Fitting errors were less than 5%.

Table 1. The EIS parameters obtained from the circuit fitting

Circuit element	R_s (Ω)	R_{ct} (Ω)	CPE (nF)	Z_w ($k \Omega s^{1/2}$)
Bare Pt electrode	7.682	1.0982×10^7	0.72126	0.53497
Pt-FeNPs electrode	83.36	1.8905×10^6	0.90192	0.8999

Results from figure 5 and Table 1 indicate that the charge transfer resistance of the FeNPs modified electrode of $1.8905 \times 10^6 \Omega$ was lower than that due to the bare electrode ($1.0982 \times 10^7 \Omega$). This indicates that the modified electrode exhibited greater conductivity than the bare one. This is so because resistance is inversely proportional to current according to Ohms Law ($V=IR$). It means the presence of the FeNPs on the platinum electrode played an important role in accelerating the transfer of electrons across the electrode interface.

3.5 Synergistic effect of coating polyaniline with FeNPs

Despite the various extensive applications of polyaniline (PANi), it has been shown that its conductivity characteristics can greatly be enhanced by doping. Doping introduces charge carriers within the polymer sub-

lattices leading to a reduction of the band gap with consequences of converting the semiconductor into an intrinsic conductor.

The electrochemistry of polyaniline in acidic media is well recorded [20-22]. In a nut shell, polyaniline is known to be a redox active polymer with accessible frontier molecular orbitals exhibiting three oxidation states. These are the leucoemeraldine peak A/A', the emeraldine peak B/B' and the most oxidized form peak C/C' [23] in figure 6 (a). Other authors have assigned this middle peak to the existence of dimmers and oligomers within the polymerization bath [24]. The electrodeposition of polyaniline was on a platinum working electrode versus a Ag/AgCl, 3M NaCl reference electrode. Cycling the potential of the working electrode varies its electrode Fermi level. When the potential of the electrode is sufficiently negative, the energy of the electrons eventually become high enough to allow them to occupy the vacant sites in the lowest unoccupied PANi molecular orbital (LUMO) [18]. This constitutes reduction. Alternatively, cycling the potential to sufficiently positive values lowers the energy of the electrode leading to the flow of electrons from the highest occupied molecular orbital (HOMO) of the PANi polymer to the working electrode [18]. This constitutes oxidation.

On placing the electrosynthesized film in 1M HCl and cycling the potential at various scan rates, only two redox peaks were evident (figure 6, b). The middle peak either merged with other peaks or disappeared all together.

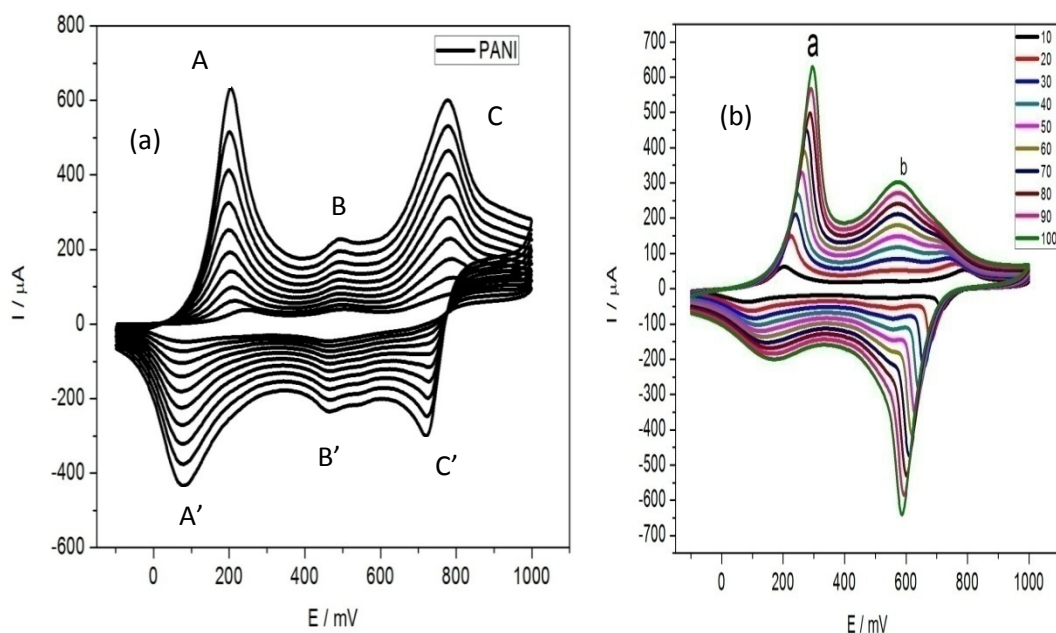


Fig. 6: Voltammogram for the electrodeposition of PANi on a platinum electrode from 1 M aniline and 100 mV/s scan rate. 1M HCl was the supporting electrolyte (a) Multi-scan rate voltammogram of the PANI film in 1 M HCl (b)

Analysis of the Pani Voltammograms indicated the peak to peak (for each redox couple) separations were greater than the expected 59 mV for a reversible system. Typical ΔE values of 150 mV for couple A/A' and about 80 mV for couples C/C' is characteristic of non-Nernstian behavior. Also the ratio of the cathodic to anodic peak currents was less than 1, ($I_{pc}/I_{pa} < 1$) further indicating quasi-reversible kinetics. Quasi-reversibility

could mean that the rate at which electrons are transferred between the Pt/PANi/solution interfaces is relatively slow. This can adversely affect its electro mediation properties in various applications.

Determination of the diffusion coefficient (D_e cm²/s) for the quasi-reversible system was done using the following equation;

$$D_e = \frac{I_p}{v^{1/2}} \times \frac{1}{FAf^{1/2}\Psi(E)} \quad (3)$$

Where; $\frac{I_p}{v^{1/2}}$ is the slope of the plot of peak current versus square root of the scan rate (diagrams not shown)

based on the polyaniline system, $f^{1/2}$ is the quantity F/RT , other symbols having their usual meaning. A slope of 2.13×10^{-3} was obtained which led to a calculation of a diffusion coefficient value of 3.25×10^{-7} cm²/s for the polyaniline (PANi/Pt system). The corresponding rate constant for the PANi/Pt system based on equation (2) was 9.52×10^{-4} cm/s which clearly indicates slow electron kinetics. The high correlation value of $r^2=0.996$ obtained indicates an electron hopping process is taking place.

On drop-coating a few microlitres of the FeNPs onto the PANi/Pt electrode and allowing a few minutes for drying, the characterization process in 1M HCl was repeated. Figure 7 shows the CV of polyaniline on platinum electrode and that of a hybrid of polyaniline/FeNPs on the same electrode at a scan rate of 10 mV/s.

Firstly, the CV for polyaniline records mainly two peaks the middle peak being barely visible. On the other hand the polyaniline/FeNPs voltammogram exhibits three distinctive peaks. A scrutiny of the PANi/FeNPs cyclic voltammogram indicates the middle couple b, have potential similar to the reversible FeNPs couple (peak a/a' in figure 3). This peak at 450 mV could be a hybrid of peak B/B' (the emeraldine peak in figure 4) and that due to the FeNPs as seen in figure 3 possibly indicating formation of a PANi/ Fe composite.

Further comparison of curve I and II shows there was a large increase in current. The current recorded for PANi/FeNPs system (curve II) at this scan rate was 6.5×10^{-5} A. That of the same peak in the absence of FeNPs was recorded to be 1.9×10^{-5} A. This means there was a near 3-fold increase in current (conductivity) as a result of incorporating FeNPs into the system. It means the FeNPs/PANi system could be a better electromediating/conducting media than the lone PANi system. The presence of FeNPs has a synergistic effect on the electromediation properties of polyaniline.

Calculation of the D_e (cm²/s) and the k^0 (cm/s) values for the new hybrid system based on equations 2 and 3 respectively gave a diffusion coefficient value of 8.76×10^{-6} cm²/s. Since the PANi diffusion coefficient was 3.25×10^{-7} cm²/s, it means there was a 27 times enhancement of the electron hopping process in the polyaniline as a result of incorporating the FeNPs. Similarly, the rate constant (k^0 , cm/s) of the PANi/FeNPs system was 9.64×10^{-3} compared to that of polyaniline of 9.52×10^{-4} recording a 10-fold improvement. Thereby inclusion of FeNPs onto the PANi system greatly improved its conductivity and electromediation characteristics.

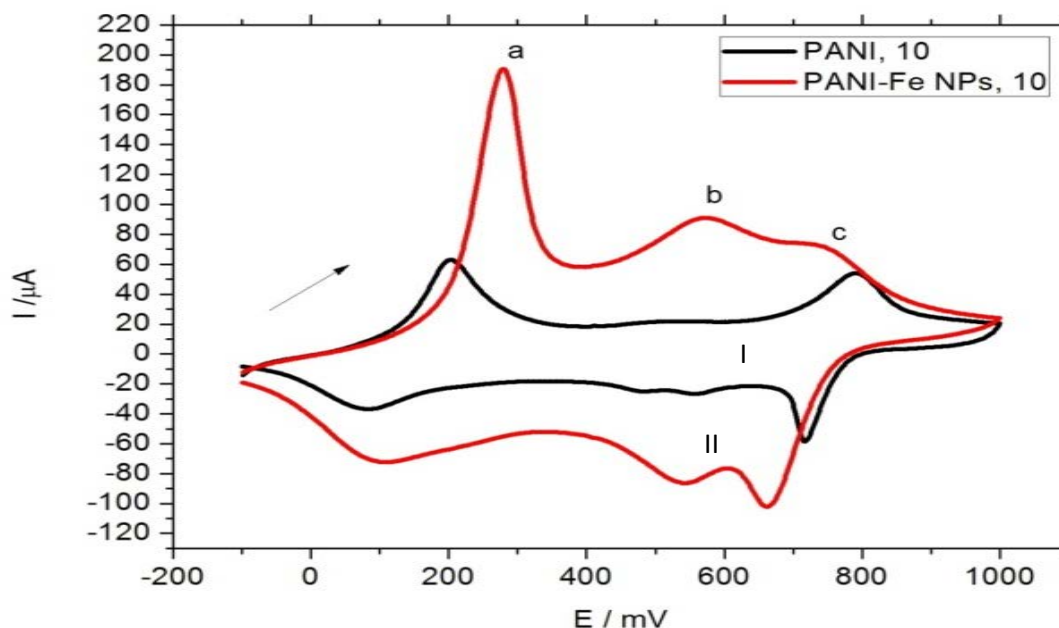


Fig. 7: Cyclic Voltammogram for Polyaniline on Pt electrode at 10 mV/s (I). Cyclic voltammograms for the polyaniline/ FeNPs hybrid on same electrode at 10 mV/s scan rate (II) highlighting synergistic effect. 1M HCl supporting electrolyte.

4. Conclusion

This work reports the successful production of iron nanoparticles (FeNPs) based on the reduction properties of green tea which has been shown to be a mixture of polyols. The latter polyols have been thought responsible for the reduction of the Fe^{3+} solution to Fe^0 nanoparticles. The presence of polyol matrices within the HRTEM results of the FeNPs indicates the stabilizing effects of the polyols that lead to the production of the free standing FeNPs. The EDX results show the presence of iron in the nanoparticles indicating successful synthesis. The diffusion coefficient (D_e , cm^2/s) and heterogeneous rate constant (k^0 , cm/s) calculated for the FeNPs were 1.44×10^{-5} and 0.028 respectively. Those for the PANi/Pt system were found to be 3.25×10^{-7} and 9.52×10^{-4} . There was slow electron transfer kinetics on the PANi. Inclusion of the FeNPs within the PANi system greatly improved its electromediation properties by several orders of magnitude.

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