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Electrochemical Synthesis of Palladium Nano Urchins Decorated Multi Walled Carbon Nanotubes for Electrocatalytic Oxidation of Hydrazine and Reduction of Hydrogen peroxide

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A facile electrochemical approach has been developed for the template free synthesis of sea-urchins like palladium (Pd) nanoparticles on multi walled carbon nanotubes (*f*MWCNTs) coated indium tin oxide electrode (ITO). The electrochemical measurements and surface morphology of the as prepared nanocomposite electrode were studied by using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and field emission scanning electrochemical microscopy (FESEM) respectively. The presence of *f*MWCNTs in the film enhances surface coverage concentration and also increases the electron transfer rate constant of the palladium nanourchins. This Pd nanourchin decorated multiwalled carbon tube modified electrode (Pd/*f*MWCNTs) exhibits a prominent electrocatalytic activity towards the detection of hydrazine and hydrogen peroxide (H_2O_2).The electrocatalytic responses of the afore mentioned analytes were measured by using cyclic voltammetry and amperometry techniques. The modified electrode also exhibits a rapid and linear electrocatalytic response for both the oxidation of hydrazine and the reduction of H_2O_2. The practical feasibility of the proposed electrode for hydrazine and hydrogen peroxide determination was evaluated in antiseptic solution and water samples as a real sample. Moreover the Pd/*f*MWCNTs exhibit excellent repeatability, reproducibility and stability for both oxidation of hydrazine and reduction of hydrogen peroxide.

Keywords: Palladium nanourchins, Multi walled carbon nanotubes, cyclic voltammetry, Amperometry, Hydrazine, Hydrogen peroxide.

1. INTRODUCTION

In recent years, studies on metal nanoparticles and organized low-dimensional nanostructures have made immense attention due to their unique capabilities to enhance mass transport, facilitate catalysis, increase surface area, and control electrode's microenvironment [1].They are also attractive for electroanalysis due to its large surface to volume ratio endows them with excellent electrocatalytic activity [2].The metal nanoparticles are prepared mainly based on reduction of metal salt in presence of reducing agent and a stabilizer. Several substrates, such as polymers, dendrimers, ionic liquids, surfactants and carbon nanotubes, have been employed as stabilizers for the metal nanoparticles [3].

Pd nanoparticles are one of the noble metals, which have their own special properties for the electrode modification process and have a enormous applications such as hydrogen storage [4], fuel cells [5, 6] and redox reactions [7].Till now well-defined morphology of solution dispersed palladium nanoparticles with different shapes are readily controlled by the templates and surfactants, but the use of surfactants and templates have some impurities and also need some organic solvents to remove the templates [8-10]. Electrochemical methods offer an easy way to fabricate well-defined nanostructured surfaces in a controlled manner. Metal nanoparticles in the shape of spheres, rods, and triangles have been successfully synthesized with such an approach [11, 12].

The extensive applications of multiwalled carbon nanotubes (MWCNTs) in various fields are due to their chemical and mechanical properties. Now a day's metal nanoparticles decorated with carbon nanotubes have been examined towards various applications such as gas sensors, nanoelectronics and heterogeneous catalysis [13].Various methods have been employed for the decoration of CNTs with palladium such as electroless deposition [14], thermal deposition [15], vapor deposition [16] and electrodeposition [17].

In this study we have successfully synthesized surfactant less and template free urchins like palladium nanoparticles by electrochemical method in 20 seconds and decorated on the *f*MWCNTs for the electrocatalytic oxidation of hydrazine and reduction of H_2O_2[18-21]. The as prepared film has been fabricated on ITO and GCE electrodes using cyclic voltammetry. The surface morphologies and the electrochemical activities of the Pd nanourchins decorated *f*MWCNTs have been carried out by using field emission scanning electron microscopy, Energy dispersive X-ray spectroscopy and electrochemical impedance analysis. The Pd nanourchins decorated *f*MWCNTs film has been successfully employed for the detection of both the oxidation of hydrazine and the reduction of H_2O_2 in lab and real samples respectively.

2. EXPERIMENTAL

2.1. Apparatus

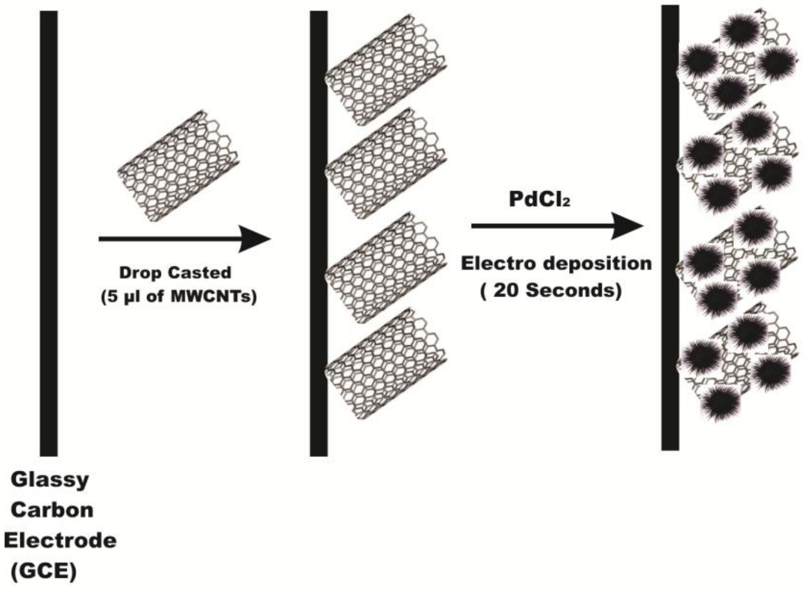
Electrochemical measurements like cyclic voltammetry (CV) were performed by a CHI 900 electrochemical analyzer and amperometric I-T was performed by CHI 900 analyzer. A conventional three-electrode cell were used at room temperature with indium tin oxide thin film coated glass electrode as the working electrode, Ag/AgCl (saturated KCl) electrode as reference electrode and a platinum wire as counter electrode. The potentials mentioned in all experimental results were referred to standard Ag/AgCl (saturated KCl) reference electrode. Surface morphology of the film was studied by FESEM (Hitachi, Japan). Electrochemical impedance studies (EIS) were performed by using ZAHNER impedance analyzer (ZAHNER Elektrik Gmbh & Co KG, Germany).

2.2. Materials

Palladium (II) chloride and multi- walled carbon nanotubes were purchased from sigma Aldrich. Hydrogen peroxide and hydrazine was purchased from wako chemicals (Japan). Hydrazine and hydrogen peroxide solutions were prepared freshly prior to the experiments. The other chemicals (Merck) that are used in this investigation were of analytical (reagent) grade (99%). All the solutions are prepared using double distilled water. Electrocatalytic studies were carried out in 0.5 M H_2SO_4. Pure nitrogen gas was passed through all the experimental solutions.

2.3. Preparation of fMWCNTs and electrochemical fabrication of Pd nanourchins decorated fMWCNTs

The purchased (commercial) MWCNTs were difficult to disperse and produce a stable homogenous solution in aqueous media due to its hydrophobic nature. Briefly, following the previous reports, the pretreatment and functionalization of MWCNTs was done by suspending 150 mg of MWCNTs in concentrated sulfuric acid – nitric acid mixture (3:1 v/v) and sonicated for 2 hr.



Scheme 1. Schematic representation of the fabrication of Pd/*f*MWCNTs composite film modified electrode.

The obtained nanotube mat was filtered by using a 0.45 mm hydrophilized PTFE membrane, further washed with deionized water until it reaches pH 7 and kept for drying under vacuum [22]. 10 mg of thus obtained *fMWCNTs* was dissolved in 10 ml water and ultrasonicated for 6 hr to get a uniform dispersion. This process not only converts *f*MWCNTs to hydrophilic nature but this also helps to breakdown larger bundles of the *f*MWCNTs into a small ones [23].

The fabrication of Pd nanourchins was synthesized by amperometric method. In a typical procedure, 5 µl of as prepared *f*MWCNTs was first drop casted on the ITO electrode, palladium nanourchins was then deposited on the *f* MWCNTs coated ITO by immersing the modified ITO in the 1.2 M HCl solution containing 28.2 mM $PdCl_2$ and the potential was kept at 0.075 V for 5 s and at 0.025 V for 15 s [24] in order to obtain the Pd nanourchins decorated multi walled carbon nanotube modified electrode (Pd/*f*MWCNTs). Then the modified electrode was rinsed with deionized water and applied for the further electrochemical studies. Scheme 1 could explain the fabrication and electron mediating properties of Pd/*f*MWCNTs nanocomposite film.

3. RESULTS AND DISCUSSIONS

3.1. Electrochemical characterization of Pd nanourchins decorated fMWCNTs

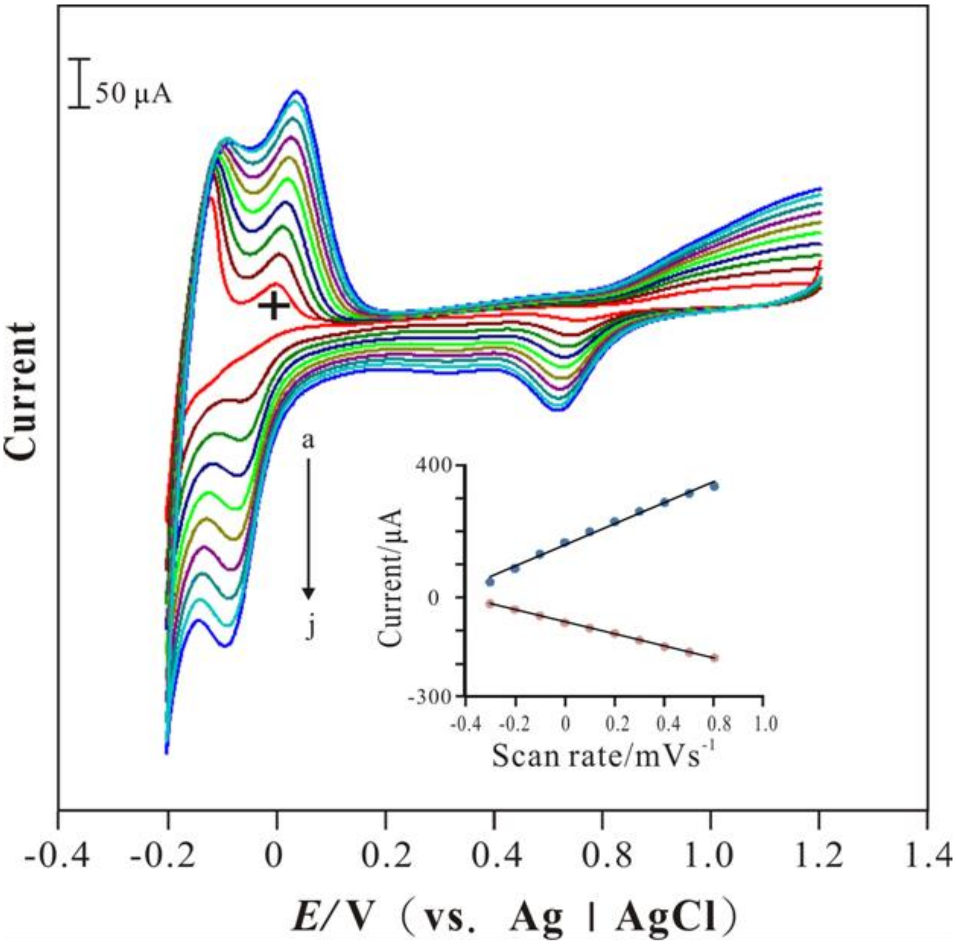


Figure 1. Different scan of the Pd nanourchins decorated *f*MWCNTs film modified electrode in 0.5 M H_2SO_4 of pH 0.01 at scan rate varies from 0.01- 0.1V/S. Inset shows a current vs. scan rate plot.

In a typical synthesis, Pd nanourchins were electrodeposited at the surface of *f*MWCNTs ITO at 0.075 V for 5 s and at 0.025 V for 15 s in quiescence solution containing 28.2 mM PdCl2 and 1.2 M HCl. Pd nanoparticles can be more readily etched in HCl electrolyte because Pd^{2+} ions are apt to form a complex ion with Cl, and the selective etching may be the reason for the urchin like nanostructure's formation. Fig.1 shows the cyclic voltammograms obtained at Pd/*f*MWCNTs composite electrode in N_2 saturated 0.5 M H_2SO_4 solution (pH 0.01) at different scan rate studies. Both Ipa and Ipc increased linearly with increase in scan rates between 0.01-0.1 Vs^{-1}.This indicated that the electron transfer process occurring at Pd/*f*MWCNTs composite film is a surface confined process. The peak currents (Ipa and Ipc) vs. scan rates plot is shown in inset of fig. 1. Both Ipa and Ipc exhibited linear relationship with scan rates, R^2 = 0.991 and 0.999, respectively.

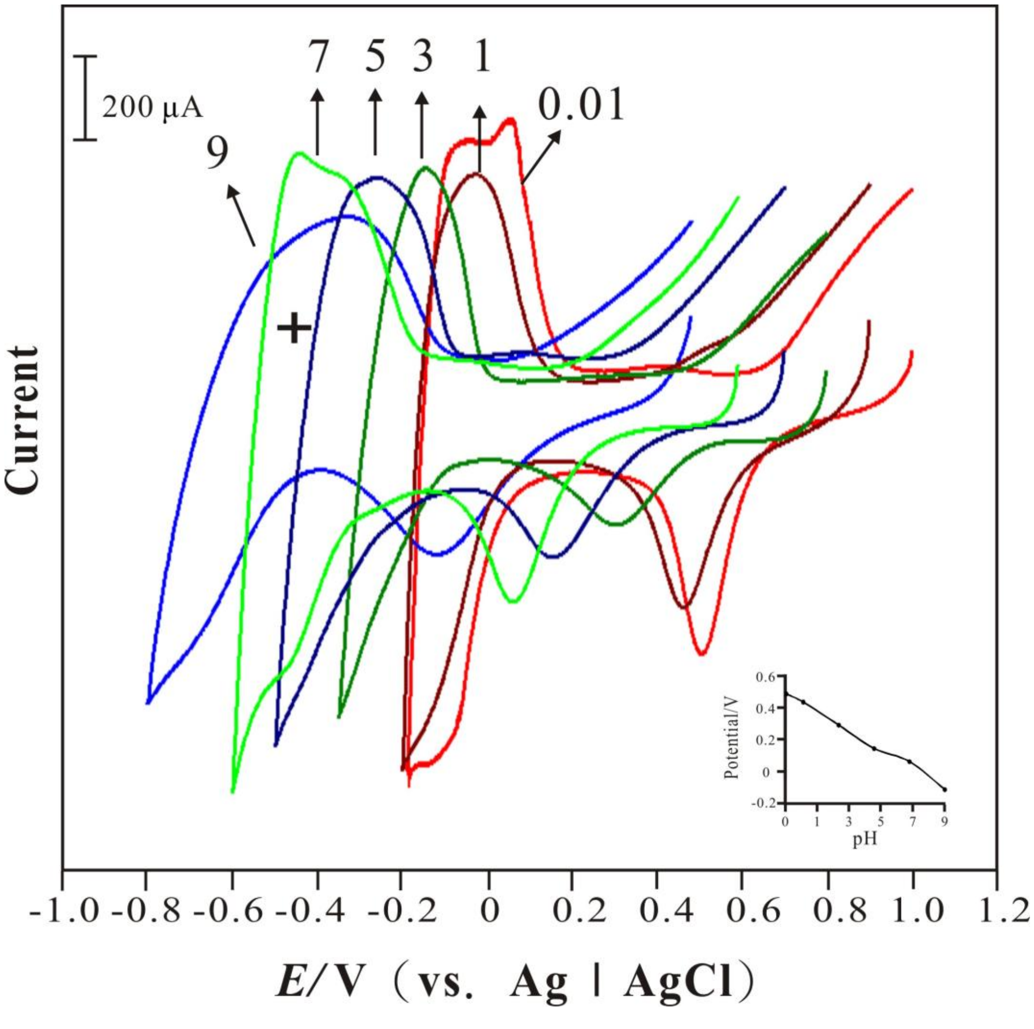


Figure 2. Cyclic Voltammograms of Pd nanourchins decorated *f* MWCNTs film modified ITO in deoxygenated different pH solutions ranging from 0.01 – 9.0 respectively. Inset shows the influence of different pH solutions vs. potential.

Fig.2 shows the effect of pH on the Pd/*f*MWCNTs composite modified film electrode in various buffer solutions (pH 0.01- 9.0). Well defined peaks were observed for the wide pH range, and the redox couples are reproducible when the modified GCE was transferred from one pH solution to the other. With increase in pH of the solutions, both these redox peaks shifted towards the negative potential. On each occasion, before transferring the modified GCE to another buffer solution the film was washed several times with doubly distilled water. However, there was no considerable decrease in the peak currents, which validates the good stability of the nanocomposite film. We have presented the influence of pH on Epa and Epc values observed at peak II in Fig. 2 inset. It is apparent that both Epa, Epc and values of the peaks exhibit a linear dependence on pH. The slope value is 69 mV/pH, which is close to the slope of 59 mV/pH for equal number of proton and electron transfer processes. Thus the Pd nanourchins decorated *f*MWCNTs involves an equal number of proton and electron transfer process.

3.2. FESEM and EDX studies

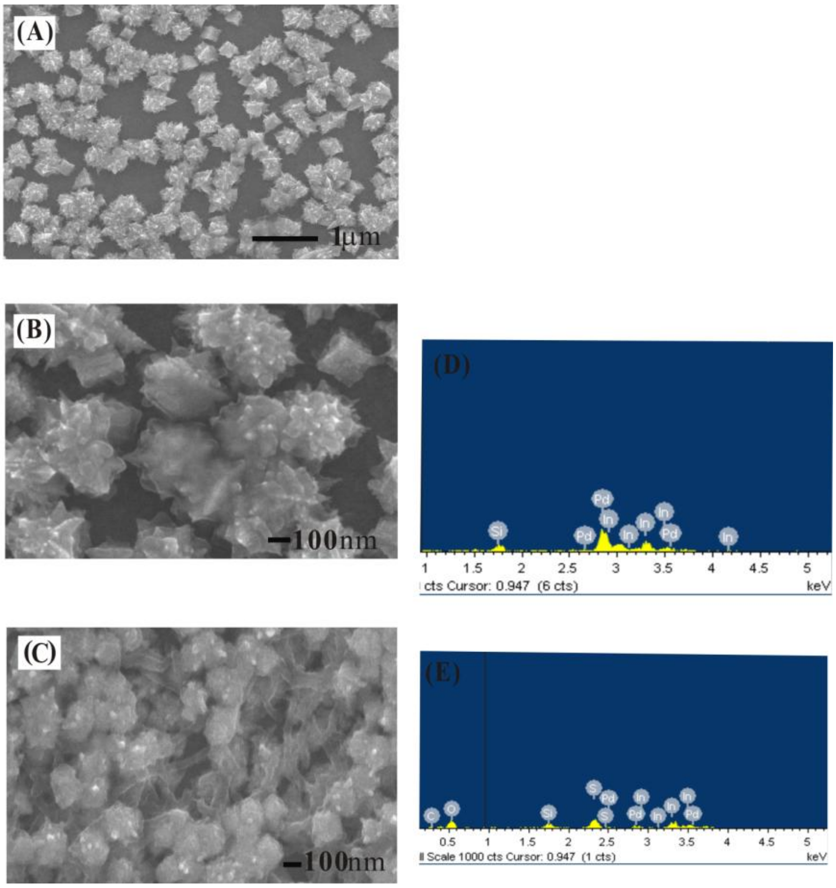


Figure 3. FESEM images and EDX spectra of Pd nanourchins (A) ,(B) and (D) at different magnifications and (C) and (E) Pd nanoruchins decoarted *f* MWCNTs film on the ITO surface.

The size and morphology of the different films were examined by FESEM. Fig.3 shows the FESEM images obtained for Pd nanourchins and Pd/*f*MWCNTs. Herein the images have been obtained for 1µM and 100 nm surface areas (view angle 90 degree). From fig.3 (A) and (B), we can clearly notice the palladium nanoparticles with spikes resemble the uniform formation of Pd nanourchins and fig.3 (B) shows the high magnification FESEM image for the formation of Pd nanourchins at the ITO surface. On the other hand, Fig.3 (C) clearly shows that the Pd nanourchins were uniformly decorated on the *f*MWCNTs. The immobilized Pd/*f*MWCNTs nanocomposite film on the surface of ITO remains stable and there are no distorted shapes. Finally from these results, it is evident that the as prepared Pd nanourchins were uniformly decorated on the *f* MWCNTs. To confirm the presence of Pd, C and O elements EDX spectral studies have been investigated for the Pd nanourchins and Pd/*f* MWCNTs films. Fig.3. (D) shows the spectral results of palladium nanourchin film contains 62.4% of Pd and the other peaks such as Si and In for the components present in the ITO electrodes. Fig.3. (E) shows the EDX spectra for Pd nanourchins decorated *f*MWCNTs film which contains the 32.62% of C and 36.56% of O and 30% Pd are present for the composite film. These results reveal that there are sufficient amount of C, O and Pd content present in the composite film.

3.3. EIS studies of different films

Impedance spectroscopy is an effective method to probe the features of surface modified electrodes [25].This study has been employed to analyze the detailed electrochemical activities of modified electrode with individual or mixed components. Here the complex impedance can be presented as a sum of the real, Z′ (ω), and imaginary Z″ (ω), components that originate mainly from the resistance and capacitance of the cell. From the shape of an impedance spectrum, the electron-transfer kinetics and diffusion characteristics can be extracted. The respective semicircle parameters correspond to the electron transfer resistance (Ret) and the double layer capacity (Cdl) nature of the modified electrode.

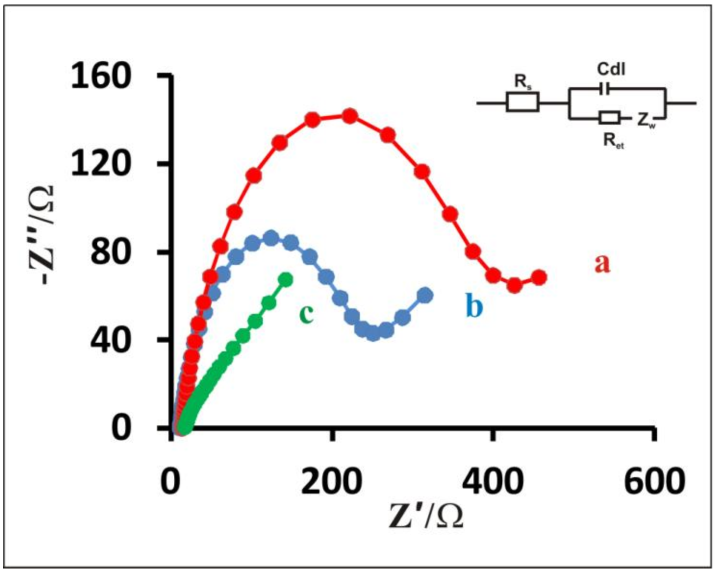


Figure 4. EIS of (a) Pd nanourchins (b) Bare and (C) Pd nanourchins decorated *f* MWCNTs modified ITO in 0.5M H_2SO_4 containing 5mM $[\text{Fe(CN)}_6]^{3-/4-}$. Inset shows the simple randles circuit model.

Fig. 4 shows the Faradaic impedance spectra, presented as Nyquist plots (Z″vs.Z′) for the Pd nanourchin film modified ITO, bare ITO and Pd/*f*MWCNTs modified ITO, respectively. The bare ITO (a) electrode exhibits a very small depressed semicircle arc, which represents the characteristics of diffusion limited electron-transfer process on the electrode surface. At the same time, the Pd nanourchin film shows like a depressed semicircle arc with an interfacial resistance due to the electrostatic repulsion between the charged surface and probe molecule Fe $(CN)_6^{3-/4-}$ (b). This depressed semicircle arc clearly indicates the capacitance behavior of the Pd nanourchin film modified ITO. Thus, the electron transfer process will become as a slow process on the Pd nanourchin film modified ITO. Whereas, in fig.4.c shows the Pd/*f*MWCNTs modified ITO exhibits a sharp line and a very small semicircle region indicating a very low impedance of the film due to the high conductivity nature of MWCNTs. These results shows that the small semicircle region for the Pd /*f*MWCNTs composite film possesses a very good electrochemical activity compare with bare and only Pd nanourchins modified ITO. Therefore, the nanocomposite film could be efficiently used for the various types of electrocatalytic reactions. Finally, based on these illustrations, the slow electron transfer kinetics nature of Pd nanourchin film and the role of *f*MWCNTs have been authenticated.

3.4. Electrocatalytic oxidation and amperometric detection of hydrazine at Pd/fMWCNTs

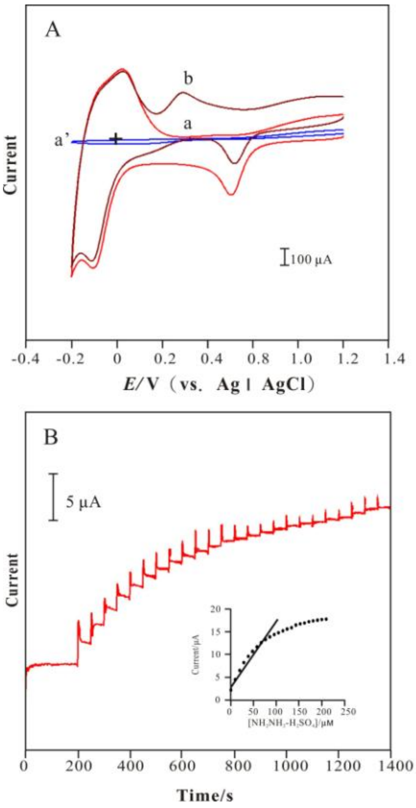


Figure 5. (A) Cyclic Voltammogram response of (a) Pd nanourchins decorated *f* MWCNTs in 0.5M H_2SO_4, (b) in the presence of hydrazine ($7*10^{-5}$ M in 0.5M H_2SO_4) and (a') at bare ITO (in 0.5M H_2SO_4). (B) amperometric i-t response of Pd nanourchins decorated *f* MWCNTs modifieed ITO for the different concentartions of hydrazine in 0.5M H_2SO_4. Inset shows a current versus concentration plot of hydrazine .

Pd/fMWCNTs nanocomposite modified film was directly employed for the detection of hydrazine. Fig.5A represents the cyclic voltammograms recorded at various electrodes in 0.5 M H2SO4 containing 70 µM hydrazine over the potential range of 0.4 to1.2 V. Curve (a) shows CV response of the modified film in 0.5 M H_2SO_4. Curve (b) displays the electrocatalytic oxidation of hydrazine at Pd/*f*MWCNTs nanocomposite film. Here, the oxidation signal of hydrazine appears at 0.277 V. At the same time, bare electrode shows diminished current response for the detection of hydrazine (curve a'). This result reveals the high sensitivity of the composite film modified electrode toward hydrazine oxidation. Although high sensitivity is achieved for hydrazine by CV, the oxidized products are adsorbed at the electrode surface and decrease the sensitivity of the electrode after each run. Therefore, the removal of the products after each run is necessary in electro analytical applications. So, amperometric technique is a more efficient method compared to CV, in which the oxidized products are thrown away by the rotating electrode, and helps the analyte to diffuse easily to the electrode surface.

Fig.5 B represents the amperometric response of hydrazine at Pd/*f*MWCNTs modified rotating disc electrode (RDE). The experiment was conducted in pH 0.01 at an applied potential of 0.27 V with a rotation rate of 1800 rpm. Hydrazine solution was added at regular intervals of time (50s). For every addition a quick response was observed and electrocatalytic oxidation of hydrazine occurs at RDE in a totally mass transfer controlled condition. The inset of fig.5b shows the calibration plot with background current correction. The linear regression equation for dependence of current with concentration of hydrazine can be expressed as $R^2= 0.8618$. The sensitivity of the electrode is 160.78 $\mu A\ mM^{-1}\ cm^{-2}$. The limit of detection was calculated as 1 µM respectively. LOD has been calculated from the formula LOD = $3S_b$ /S, where, S_b is the standard deviation of blank signal and S is the sensitivity of the electrode. A satisfactory hydrazine quantification results have been achieved for the Pd/*f*MWCNTs composite film and they also possess a good stability towards the oxidation of hydrazine.

3.5.Amperometric and electrochemical detection of H_2O_2 at Pd nanourchins decorated fMWCNTs

Electrochemical detection of H_2O_2 has been examined by CV (fig. 6(A)). In fig. 6(A) curve (a) shows CV response of the modified film in 0.5 M H_2SO_4. Curve (b) shows the detection of H_2O_2 (190 µM) at Pd/*f*MWCNTs nanocomposite film. The electrochemical reduction signal of H_2O_2 appears at -0.088 V on the Pd nanourchins *f*MWCNTs modified film in 0.5M H_2SO_4. Bare (curve a') showed the null response for the detection of H_2O_2. The above result clearly shows that the Pd nanourchins decorated *f*MWCNTs composite film shows excellent response for the detection of H_2O_2 in 0.5 M H_2SO_4. Based on this examination further we have employed the modifed film for the amperometric detection. Fig.6 B shows the amperometric i-t curve recorded for Pd nanourchins decorated *f*MWCNTs modifed film upon various H_2O_2 concentration additions in N_2 saturated 0.5M H_2SO_4. The electrode potential was kept constant at -0.088V. The modifed film shows a rapid and well defined amperometric response with maximum current response towards each addition of H_2O_2. It shows a good reduction current response within 5 sec. The linear range dependence of amperometric response on concentration is expressed as I (µA) = 891002 C (mM) +38.342 , R^2 = 0.9817. Based on the calibration plot , the detection limit and linear range for the proposed electrode for H_2O_2 detection was found as 0.1 µM and 1* 10^{-6}- 1.9 * 10^{-5} M. A satisfactory H_2O_2 quantification results have been achieved for the Pd nanourchins decorated *f*MWCNTs film and they also posses a good satbility for the reduction of H_2O_2.

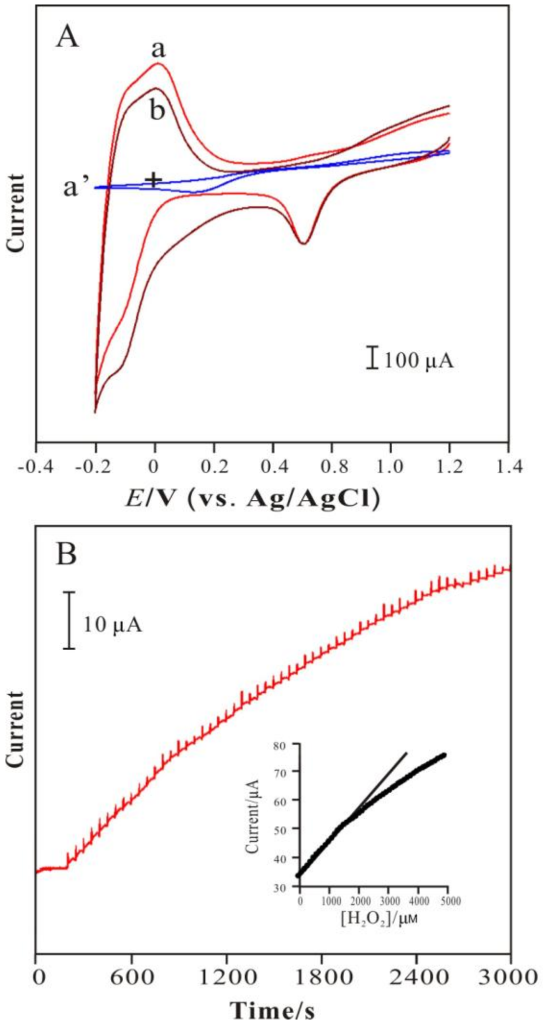


Figure 6. (A) Cyclic Voltammogram response of (a) Pd nanourchins decorated *f* MWCNTs in 0.5M H_2SO_4, (b) in the presence of H_2O_2 (1.9* 10^{-5}M, in 0.5M H_2SO_4) and (a') at bare (1.9* 10^{-5}M in 0.5M H_2SO_4). (B) Amperometric i-t response of Pd nanourchins decorated *f* MWCNTs modifieed ITO for the different concentartions of H_2O_2 in 0.5M H_2SO_4. Inset shows a current versus concentration plot of H_2O_2.

3.5. Real sample analysis for H_2O_2 and Hydrazine

To investigate the practicality of Pd/*f*MWCNTs nanocomposite film for feasible usage, the concentration of H_2O_2 in antiseptic solution (30% H_2O_2) was examined. Here the dilution of real samples was employed with 0.5 M H_2SO_4 to bring the H_2O_2 content with those shown in the table1. The real sample results for the antiseptic solution (using standard addition method) are listed in table 1.

Furthermore, spiked water samples also studied for the practical application of the fabricated nanocomposite film towards hydrazine determination. Hydrazine was spiked into the water samples collected from the tap water.

Table 1. Determination of H_2O_2 in antiseptic solutions at Pd/*f*MWCNTs nanocomposite film

Samples	Added	Found	Recovery
1	2.0 µM	2.05 µM	102.5
2	3.0 µM	2.93 µM	97.66
3	80 µM	78.7 µM	98.37
4	100 µM	101.5 µM	101.5

The spiked samples were analyzed using Pd/fMWCNTs nanocomposite film by amperometry. The comparison of the spiked values and the determined values were listed in Table 2. Thus, the agreeable recoveries were obtained by using the Pd/fMWCNTs nanocomposite film confirms that the proposed film is also suitable for the real sample analysis.

Table 2. Determination of Hydrazine in water samples at Pd/*f*MWCNTs nanocomposite film

Samples	Added	Found	Recovery
1	3.2 µM	3.1 µM	96.8
2	34.9 µM	34.8µM	99.7
3	52.3 µM	54.0 µM	103

3.6.Repeatability, reproducibility and Stability studies

The Pd nanourchins decorated *f*MWCNTs composite film for the detection of hydrazine and H_2O_2 the RSD value was found as 4.5 %. Further the reproducibility for the detection of hydrazine and H_2O_2 was carried out using five glassy carbon electrodes and the RSD value was found as 3.22%. The repeatability and the reproducibility values confirm that the proposed film was suitable for the detection and determination of hydrazine and H_2O_2. Next the stability of the film has been examined by storing it at the room temperature in the open air condition (Figure not shown). It was stable for four weeks a gradual decrease (15%) has been found from the current initial values. we can conclude that the film was more active and stable in open air condition and there is few gradual decrease in the back ground current response.Further by increasing the number of cycles and other factors, we can improve the stability of this type of electrodres. Afterwards, we attempt to investigate the operational stability of the modified film in the presence of both hydrazine and H_2O_2 individuall into continuously stirred (1800 RPM) at the applied potential for each analyte . Even after continously operated for 3000 s, the response current decreased only by 7 %, indicating the excellent operational stability of the modified film. Thus, both storage and operational stabiliies are appreciable owing to the stability of the Pd/fMWCNTs nanocomposite film.

4. CONCLUSIONS

This work demonstrates the electrochemical synthesis of template free Pd nanourchins decorated *f*MWCNTs using Cyclic Voltammetry within twenty seconds and used for the electrocatalytic oxidation of hydrazine and reduction of H_2O_2. Fabricated nanoparticles were examined by FESEM analysis. This study shows that , as prepared palladium nanourchins were decorated on the *f*MWCNTs. The electrochemical activities of the Pd nanourchins decorated *f*MWCNTs composite film have been examined using CV and EIS analysis. The proposed composite film were employed for the detection electrochemical oxidation of hydrazine and reduction of H_2O_2 by amperometric technique. Based on these results, we conclude that the Pd nanourchins decorated *f*MWCNTs modified film provides good conductivity and stability and exhibits promising electrocatalytic activity and rapid response towards hydrazine and H_2O_2.

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