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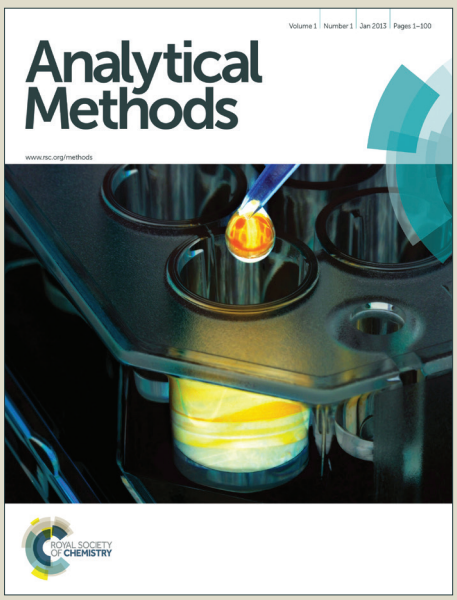

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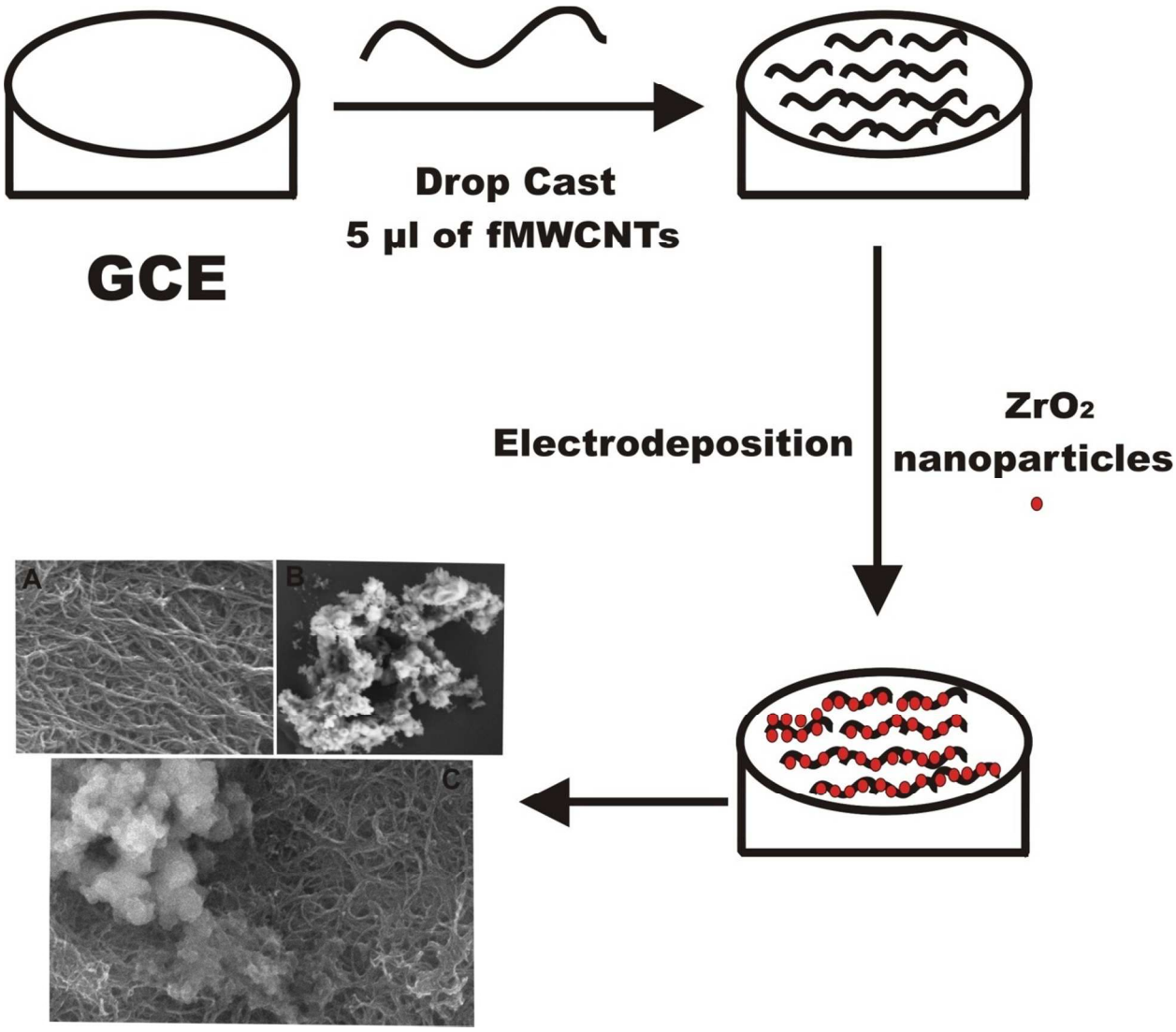
Graphical Abstract



Electrochemical fabrication *f*MWCNTs/ZrO_2 nanocomposite film on the glassy carbon electrode electrode surface.

A Novel voltammetric p- nitro phenol sensor using ZrO_2 nanoparticles incorporated multiwalled carbon nanotubes modified Glassy carbon electrode.

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Abstract

Here in, we report zirconium oxide (ZrO_2) nanoparticles incorporated functionalized multi walled carbon nanotubes (*f*MWCNTs/ZrO_2) nano composite via an in situ, simple and clean strategy on the basis of the electrochemical redox reaction of Zirconyl chloride ($ZrOCl_2$). The electrocatalytic measurements and surface morphology of the as prepared nanocomposite were studied using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and field emission scanning electron microscopy (FESEM) respectively. The as prepared ZrO_2 incorporated *f*MWCNTs nanocomposite modified GCE (*f*MWCNTs /ZrO_2) exhibits a prominent electrocatalytic activity towards the voltammetric determination of p- nitrophenol. The presence of *f*MWCNTs in the film enhances the surface coverage concentration and also increases the electron transfer rate constant, of the ZrO_2 nanoparticles. The modified electrode shows the linear range of 2 to 26 µM for p-nitrophenol. The proposed film also successfully used for the voltammetric detection of p-nitrophenol in river and tap water samples with a linear range of 0 to 24 µM. A well-defined Peak for the detection of p-nitrophenol in water samples has proven this *f*MWCNTs/ZrO_2 modified electrode as a successful sensor material. Moreover, the proposed film has long term stability towards p-nitrophenol sensor.

Key words: Zirconium nanoparticles,Functionallized multi walled carbon nanotubes ,p-nitrophenol, Voltammetric determination, water samples.

1. Introduction

Recent years, studies of nanoparticles and well organized low-dimensional nanostructures having overwhelming attention due to their unique capabilities to enhance mass transport, facilitate catalysis, increase surface area, and control of electrode's microenvironment[1]. Nevertheless, they also have fascinating consideration towards electroanalysis owing to its large surface to volume ratio endows them with excellent electrocatalytic activity.[2] Nonetheless , here the ZrO_2 nanoparticles are an inorganic oxide, which have been demonstrated as an ideal material for the immobilization of biomolecules with oxygen containg groups because of its thermal stability, chemical inertness, lack of toxicity, and affinity for the groups containing oxygen.[3] However, these nanoparticles also provide a three-dimensional stage, and some of the restricted orientations, which is tailored to the direct electron transfer between the protein molecules and the conductor surface.[4]Owing to its atractive properties, ZrO_2 mainly involved in electrochemcial sensor applications. In recent years, composite of $ZrO_2$with carbon material has applied to the chemical and biosensor application [5,6]. On the other hand, 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 grateful attention for various applications such as gas sensors, nanoelectronics and heterogeneous catalysis.[7]So for various methods have been employed for the decoration of CNTs with nanoparticles such as electroless deposition,[8] thermal deposition,[9]vapor deposition,[10] and electrodeposition.[11]Moreover nowadays the nanoparticles decorated with CNT modified electrode has grateful consideration to electrochemical sensor applications[12,13].

On the other hand, Nitro phenols (NPs) are a class of anthropogenic, toxic, inhibitory and bio refractory organic compounds. These kinds of NPs are used extensively in the production of

pesticides, dyes and pharmaceuticals. In particular, p-nitrophenol (p-NP) is one of the toxic derivatives of the parathion insecticide, which is considered to be hazardous wastes and priority toxic pollutants by US Environmental Protection Agency (EPA).[14] Hence detection of the p-NP requirements not only in industrial waste waters but also in freshwater and marine environments. Owing to its high stability and solubility in water, the degradation treatment of waste waters contaminated with p-NP by traditional techniques is difficult and generally requires a long period of incubation. Therefore, it is extremely importance to develop simple and effective methods for trace analysis of p-NP in aqueous solutions to monitor the degradation process of p-NP or to protect water resources and food supplies [15, 16].

Electrochemical methods [17–21] have received considerable attention in the determination of NPs because of their great advantages, such as simple operation, fast response and in situ detection, over to chromatographic methods [22]and spectroscopic ones respectively. Consideration of selectivity and sensitivity in electrochemical detections are strongly dependent on microstructures and properties of electrode materials. So far few researchers are focusing on these nanostructured materials[23] or chemically modified electrodes [24,25] in electrochemical sensors. Herein, we report a simple electrodeposition method to prepare *f*MWCNTs / ZrO_2 nanocomposite modified electrode. The redox complex with the nano structure materials was employed for the selective electrocatalytic determination of p-NP by making *f*MWCNTs/ZrO_2 nanocomposite. This composite was prepared on GCE and ITO electrodes by simple two steps process by drop casting of *f*MWCNTs followed by electrochemical reduction in the zirconyl chloride solution in PBS pH 7. As prepared nanocomposite electrode was characterized using surface analysis technique FESEM along with electrochemical techniques CV and EIS. The

*f*MWCNTs/ZrO_2 modified electrode successfully determine p-NP wthout any interference and quantified in real system in different water samples.

2. Experimental

2.1 Apparatus

An electrochemical measurement, cyclic voltammetry (CV) and Linear sweep voltammetry was performed by a CHI 1205A electrochemical analyzer. A conventional three-electrode electrochemical cell was used at room temperature, which consist of glassy carbon electrode (GCE) (surface area = 0.07 cm^2) 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).

Materials

Zirconyl chloride octahydrate, multi- walled carbon nanotubes and p- nitro phenol were purchased from sigma Aldrich. p – Nitro phenol solution were freshly prepared every day. The other chemicals (Merck) that are used in this investigation were of analytical grade (99%). Water samples were collected from nearby river, likewise the tap water was collected from lab. All the solutions were prepared using double distilled water. Electrocatalytic studies were carried out in 0.05 M pH 7 PBS. Pure nitrogen gas was purged through all the experimental solutions for removing dissolved oxygen.

2.2 Preparation of *f*MWCNTs and electrochemical fabrication of ZrO_2 nanoparticles incorporated *f*MWCNTs nanocomposite modified electrode

The pristine (commercial) MWCNTs were difficult to disperse and produce a stable homogenous solution in aqueous media due to its hydrophobic nature. So it's necessary to convert into hydrophilic nature using acid treatment. Briefly, following the previous reports, the pretreatment and functionalization of MWCNTs was made by suspending 150 mg of MWCNTs in concentrated sulfuric acid – nitric acid mixture (3:1 v/v) and sonicated for 2 hour. The obtained nanotube mat was filtered by using a 0.45 mm hydrophilized PTFE membrane, filtered and further washed with deionized water until it reaches pH 7 and kept for drying under vacuum.[23] 10 mg of thus obtained *fMWCNTs* was dissolved in 10 ml water and ultrasonicated for 6 hrs. 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. [24]

The ZrO_2 modified GCE was prepared by simple electrochemical deposition method. In a typical procedure, 5 µl of as prepared *f*MWCNTs was drop casted on the glassy carbon electrode (GCE) and dried in air oven at 30° C. Then the *f*MWCNTs was placed into the electrochemical cell containing 4 ml 5.0 mM $ZrOCl_2$ in 0.05 M pH 7 PBS solution. 10 consecutive cyclic voltammetric cycles were recorded in the potential range between 0.7 and -1.1 V at the scan rate of 20 mV/s to obtain stable voltammogram.[25] The resulting *f*MWCNTs/ZrO_2 film modified GCE was then rinsed with double distilled water and used for further electrochemical studies.

3. Results and Discussion

3.1 Electrochemical characterization of fMWCNTs/ZrO_2 nanocomposite film modified GCE

Fig. 1 shows the cyclic voltammetric (CV) deposition process of ZrO_2 nanoparticles on *f*MWCNTs modified GCE. It can be seen that in figure 1, the obvious reduction peak appeared at first cycle, indicating reduction process of $ZrOCl_2$. During the normal electro deposition, linear increasing current upon repetitive scanning is observed. The steep rise in the cathodic and anodic current at the potential range of 0.7 to -1.1 V corresponds to the complex redox behavior of $ZrOCl_2$ on the *f*MWCNTs modified surface. The formation of ZrO_2 on the electrode surface can be expressed by the following reaction mechanism.

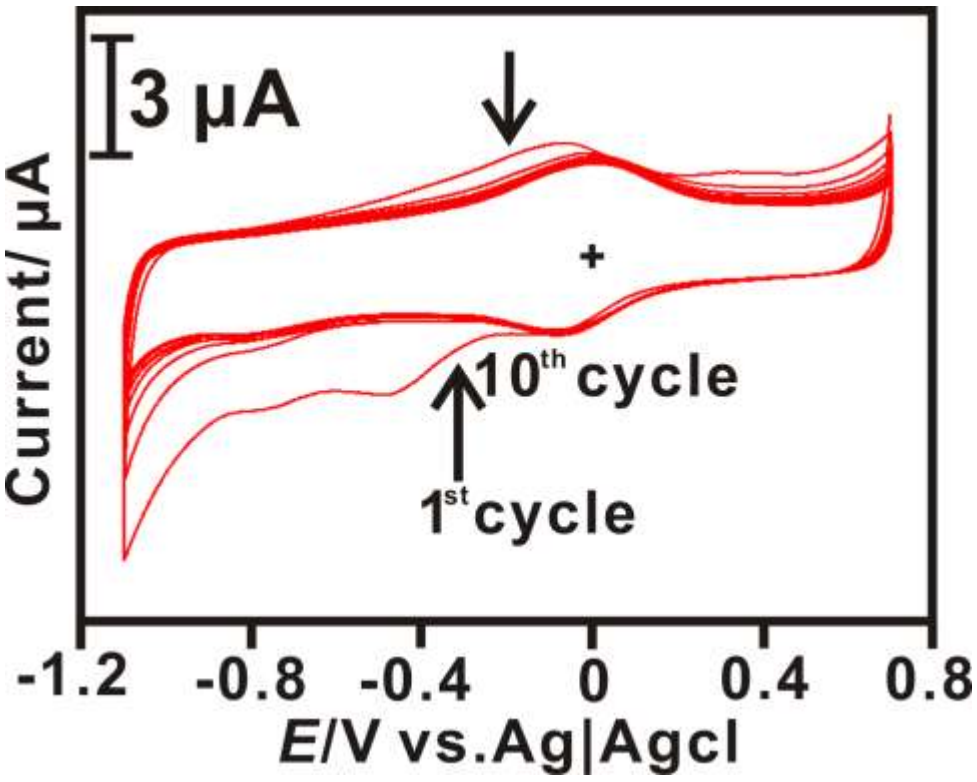


Fig.1.Cyclic Voltammograms of electrodeposition of ZrO_2 nanoparticle on *f*MWCNTs glassy carbon electrode at pH 7 PBS containing (5×10^{-3}M) $ZrOCl_2$. Potential scan between 0.7 to -1.1 V for ten cycles at the scan rate of 20 mV/s.

$$ZrOCl_2 + e^- \rightarrow ZrOCl + Cl^- \quad (1)$$

$$2ZrOCl + 2H_2O \rightarrow 2ZrO_2 + 2HCl + H_2 \quad (2)$$

In the next step, the prepared *f*MWCNTs/ZrO_2 nanocomposite modified electrode was transferred into pH 7 PBS for scan rate studies. Fig.2 shows the cyclic voltammograms obtained at *f*MWCNTs/ZrO_2 composite electrode in N_2 saturated PBS solution (pH 7) at different scan rate studies. Ipa increased linearly with increase in scan rates between 0.01-0.1 V/s. This indicated that the electron transfer process occurring at *f*MWCNTs/ZrO_2 composite film is a surface confined process. The peak currents (Ipa) vs. scan rates plot is shown in fig. 2 inset. Ipa exhibites linear relationship with scan rates, $R^2 = 0.998$ respectively.

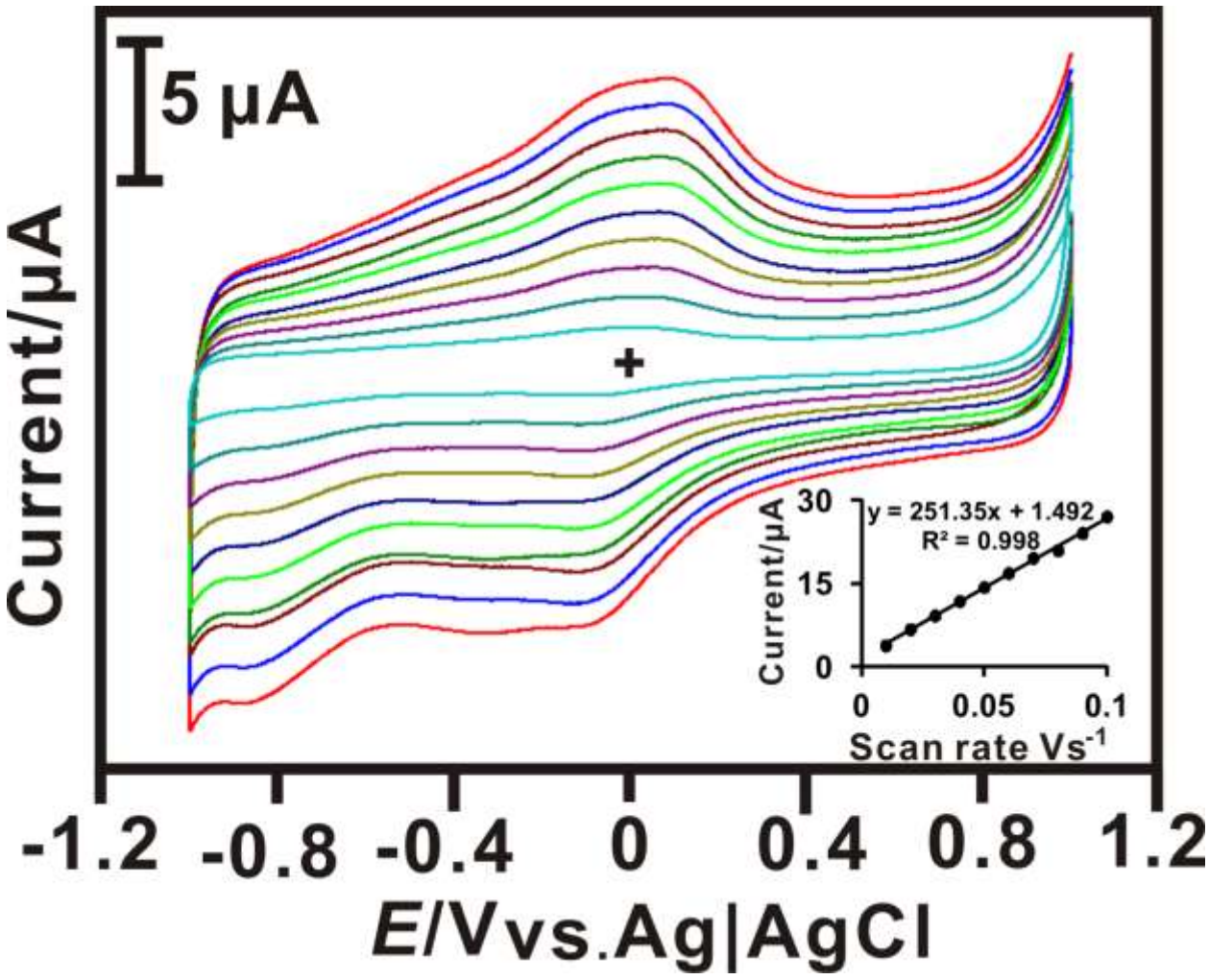


Fig.2.Different scan rate studies of the GCE/*f*MWCNTs /ZrO_2 modified electrode in pH 7 at scan rate varies from 0.01 to 0.1 V/S. Inset shows a current vs. scan rate plot at pH7.

3.2 Investigation of electrochemical behavior of various film modified electrodes using EIS studies

The EIS has been studied to analyzing the Nyquist plots of the modifled films. Randles equivalent circuit model was carried out to fit the experimental parametrs, such as electron transfer resistance (Ret), solution resistance (Rs) and double layer capacity (Cdl). Fig.3. shows the real and imaginary part of electrochemical impedance spectra for the bare and

*f*MWCNTs/ZrO_2 nanocomposite modified GCE were recorded in 5 mM [Fe (CN) $_6$] $^{3-/4-}$ in pH 7 PBS. The semicircles obtained at lower frequency indicates the diffusion limited electron transfer process and charge transfer limited process for the higher frequency. Fig.3 (a) represents the nyquist plot for the *f*MWCNTs/ZrO_2 nanocomposite film. As shown in the figure, *f*MWCNTs/ZrO_2/GCE exhibits a small semicircle region with a very low electron transfer resistance value (Ret = 50(Z'/Ω)) indicating rapid electron transfer of the film due to the high conductivity nature of *f*MWCNTs and (b) bare GCE exhibits a large semicircle with a high electron transfer resistance value of ((Ret = 175(Z'/Ω)).This results shows that the small semicircle region for the *f*MWCNTs /ZrO_2 nanocomposite film possess a very good electrochemical activity compare with bare GCE .Therefore, the composite film could be efficiently used for the various types of electrocatalytic reactions.

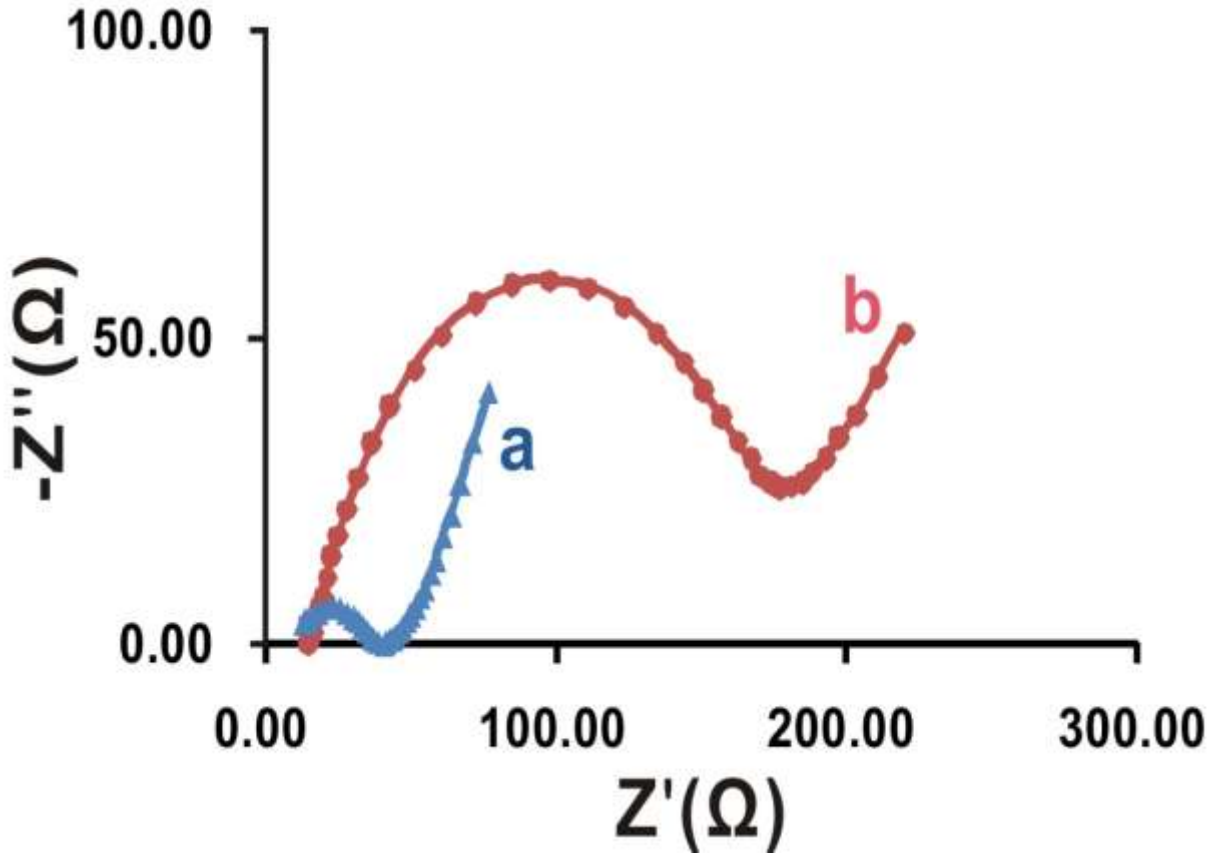


Fig.3.EIS of a) GCE/*f*MWCNTs /$ZrO_2$and b) bare GCE in 5mM [Fe (CN) $_6$]$^{3-/4-}$ in pH7 PBS.

3.3 Effect of pH

The effect of pH on the *f*MWCNTs/ZrO_2 modified electrode was investigated in phosphate buffer solutions with different pH values ranging between pH 1 to 13 (Fig.4). As shown in figure 4A the anodic and cathodic peak potential was shifted negative side with increases in the pH of the solution (from 1 to 13). The plot of pH vs. E^0 (inset fig) exhibits linear dependence over the whole pH. The linear regression equation has been written as, E^0 (V) = 0.3957 (V) -0.056 pH (V/pH). Here, the slope value of -0.056 V/pH nearly closed with theoretical value (-0.058 V/pH) for reversible process having equal number of electrons and protons. The *f*MWCNTs/ZrO_2 shows

well-defined, stable and enhanced redox peaks in pH 7 (inset of Fig.4); therefore we select pH 7 for all our electro catalytic experiments.

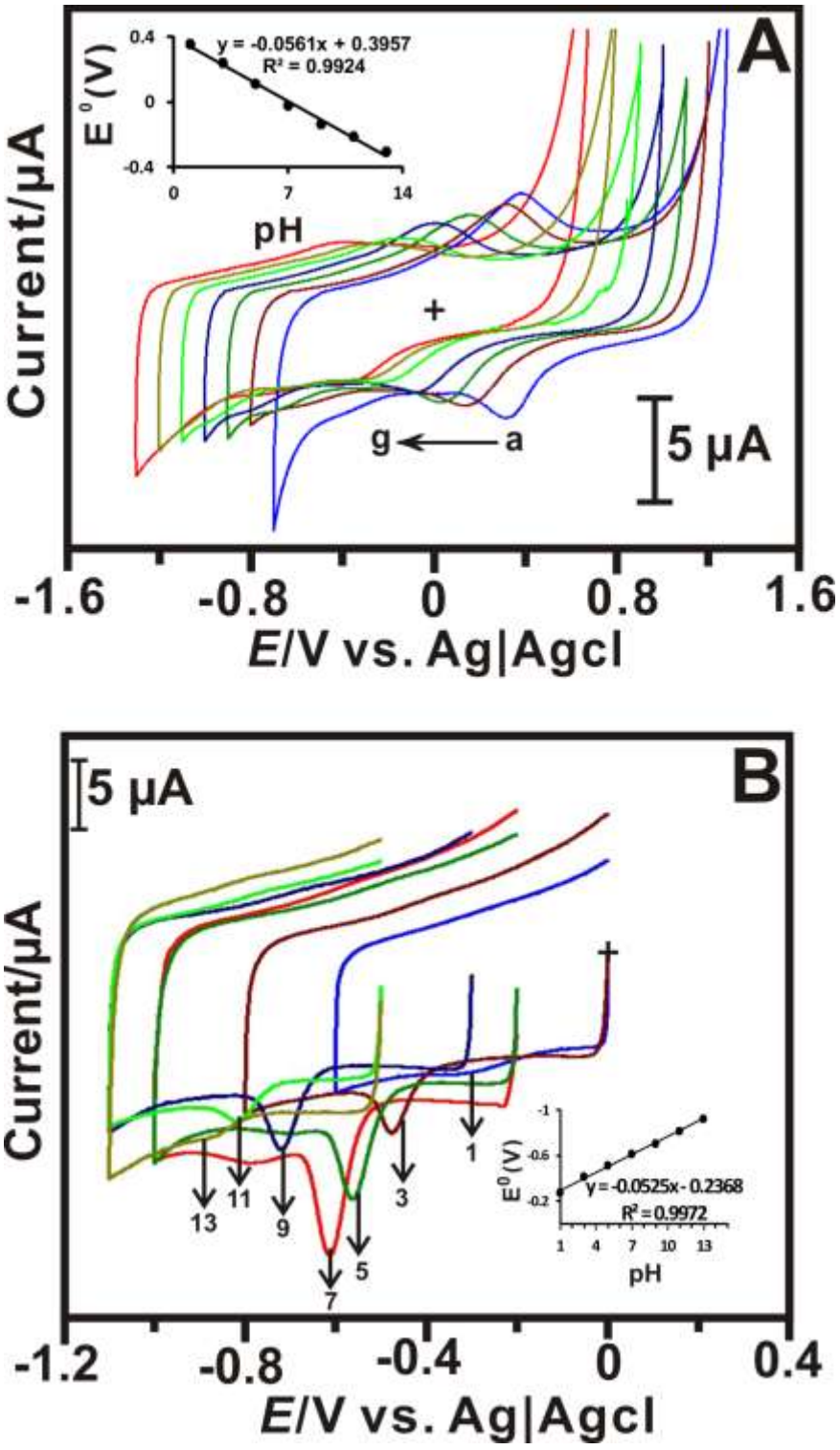


Fig.4. A) Cyclic Voltammogram of ZrO_2 nanoparticles incorporated *f*MWCNTs film modified GCE in deoxygenated different pH solutions ranging from 1 – 13 respectively. Inset shows the influence of different pH solutions vs. potential B) CV of GCE/*f*MWCNTs /ZrO_2 in different pH containing 25 µM of p-nitrophenol.

Figure 4B shows the CV of p-nitrophenol (25 µM) catalytic reduction in different pH solution at 50 mV/s. As shown figure well enhanced redution peak was observed at pH 7 PBS solution. Moreover the redution peak potential shifted towards more negative potential side in basic pH solution. At same time the peak potential move towards more positive potential side at acidic solution. Nevertheless, at lower pH (pH 1) very small redution peak was observed. This results indicates that the p-nitrophenol redution reaction was pH dependent reaction. The linear regression equation based on the calibrtaion plot was found as E^0 (V) = 0.291(V) -0.052 pH (V/pH). Hence we conclued that to carry out all electrocatylic studies on pH 7.

3.4 Morphological studies

The figure 5 (A – C) shows the FESEM images of *f*MWCNTs, ZrO_2 and *f*MWCNTs/ZrO_2 coated on Indium tin oxide (ITO) electrode. It can be seen from Fig.5.A, bundles of *f*MWCNTs with uniform thickness of 3-4 nm having tubular network. Fig.5 B shows the spongy like ZrO_2 nanoparticles coagulated each other over the ITO surface. Fig.5C shows the image of the *f*MWCNTs/ZrO_2 on the ITO substrate in which the ZrO_2 nanoparticles are homogenously incorporated throughout the tubular network of nanotubes and the distribution of the nanoparticles are almost uniform throughout the nanotubes layer . Finally from these results, it is clearly evident that the electrodeopisted ZrO_2 nanoparticles were uniformly incorporated on the *f*MWCNTs.

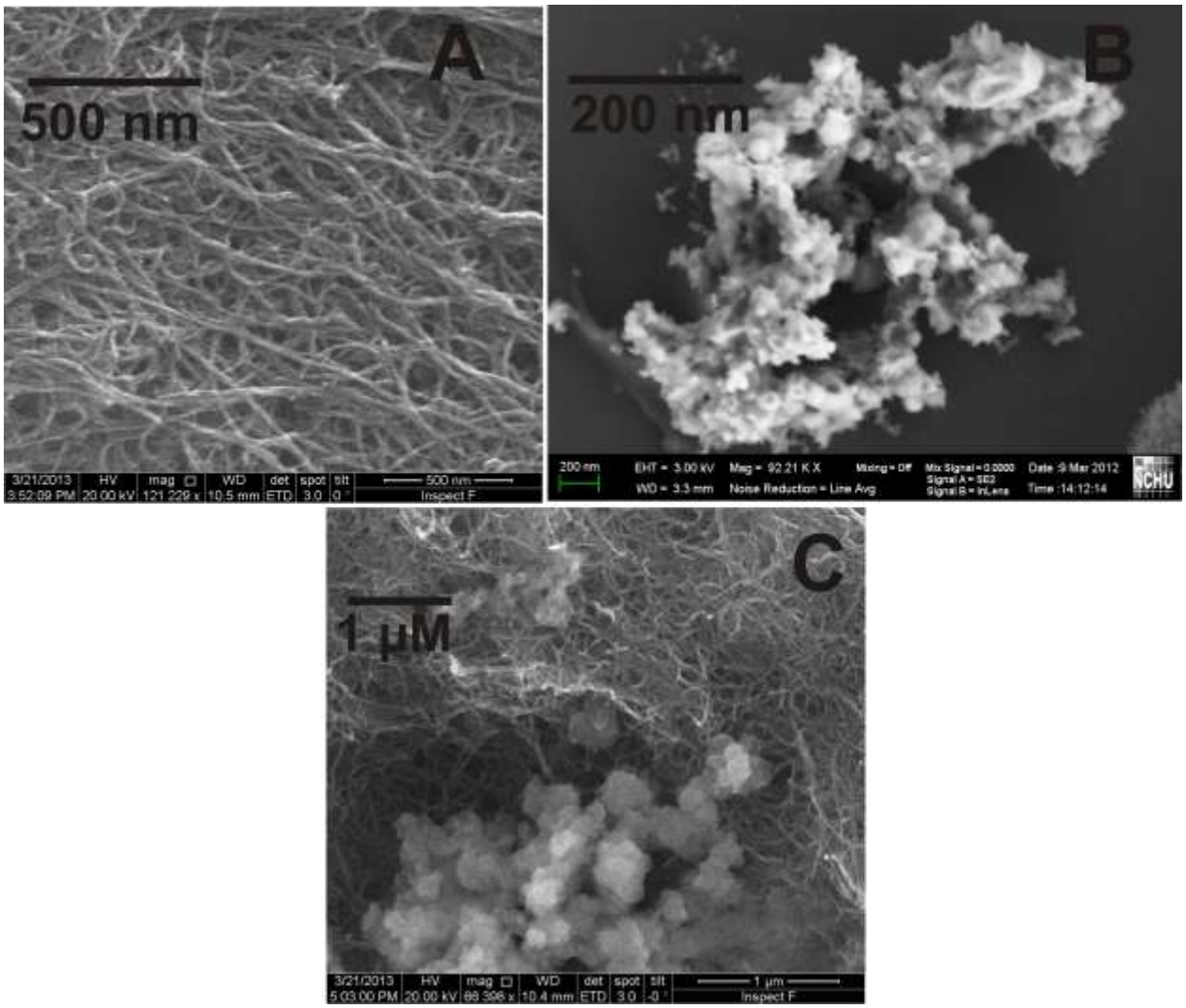
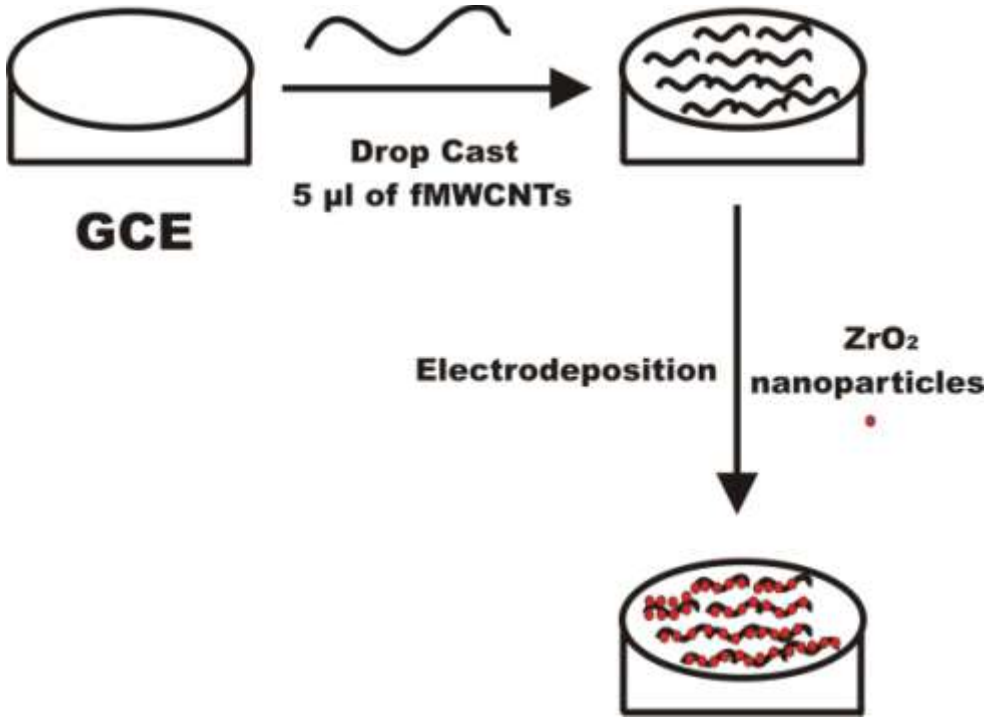


Fig.5.FESEM images of (A) *fMWCNTs*, (B) ZrO_2 and (C) *f*MWCNTs/ZrO_2 films at different magnifications.

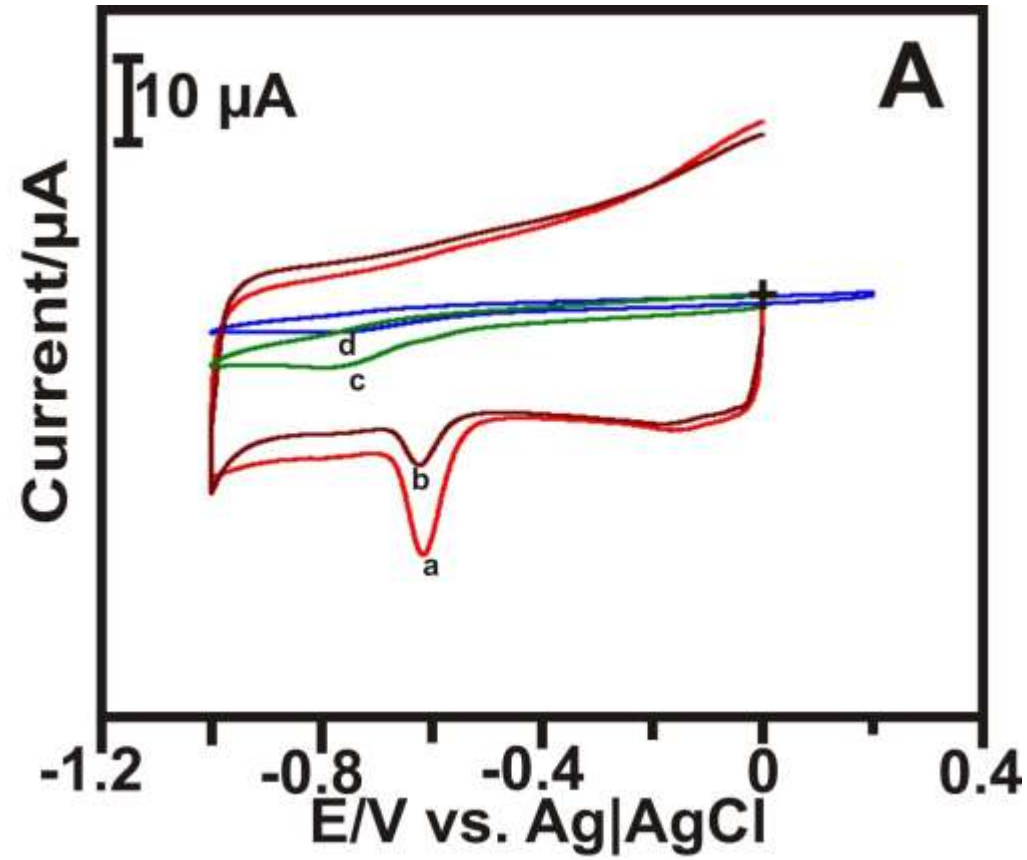
3.5 Voltammetric determination of p-nitrophenol at fMWCNTs/ZrO_2 nanocomposite modified electrode

The *f*MWCNTs/ZrO_2 nanocomposite modified GCE could be directly employed for the voltammetic detection of p-nitrophenol. It can be seen that, relative to the bare GCE, *f*MWCNTs/ZrO_2 nano composite modified GCE (figure 6A) shows well defined obvious electrocatalytic peaks for the detection of p-nitrophenol (peak a) .At the same, only *f*MWCNTs

modification gives separate peaks which were not as obvious as found using *f*MWCNTs /ZrO_2 film(peak b). It is worth, noting that *f*MWCNTs/ZrO_2 /GCE exhibits p-nitrophenol reduction peak potential roughly 150 and 180 mV less potential than ZrO_2 /GCE (peak c) and bare GCE (peak d). Finally, this CV results clearly depict the capability of the proposed *f*MWCNTs/ZrO_2 film for the detection of p-NP.This may be due to the presence of ZrO_2 nanoparticles which acts a electroactive centers for the detection and determination of these compounds, In addition, the combination of *f*MWCNTs as another layer on the surface clearly supports the surface enhancement and as well as selective detection p-NP. Scheme 1 could explain the fabrication *f*MWCNTs/ZrO_2 nanocomposite film on the electrode surface.



Scheme 1. *Schematic representation of single step fabrication of fMWCNTs/ZrO_2 nanocomposite modified electrode.*



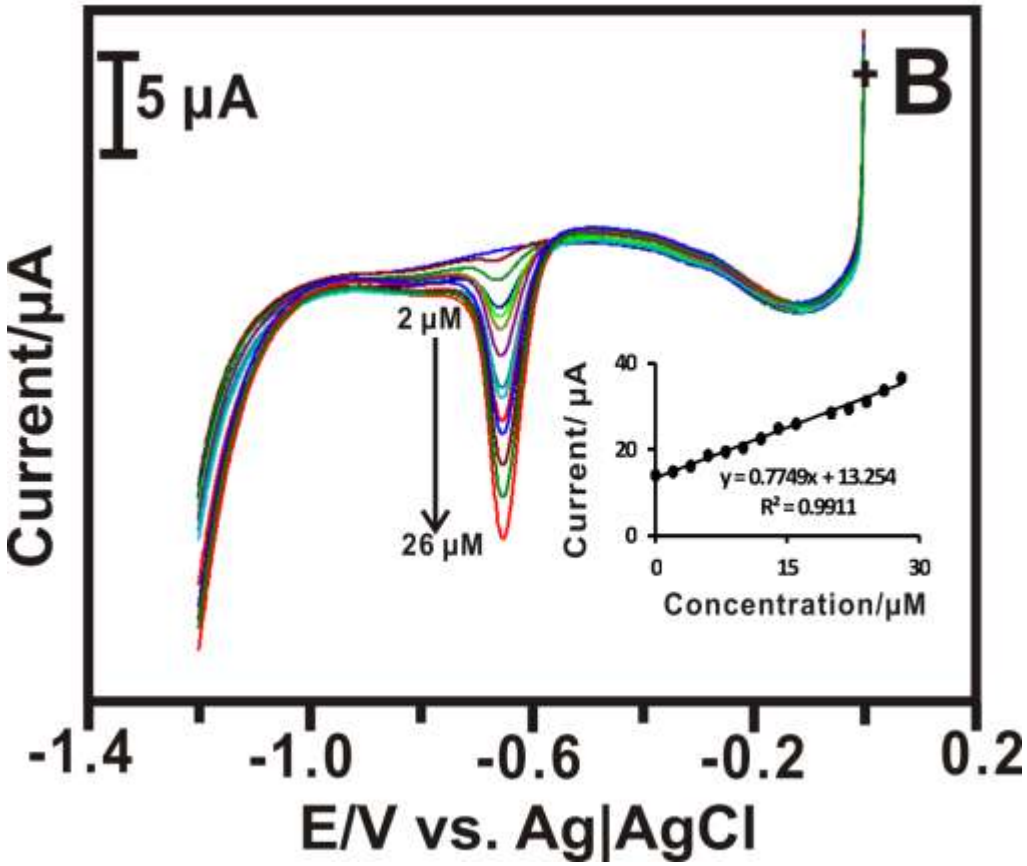


Fig.6.A) CV obtained at a) *f*MWCNTs/ZrO_2 b) *fMWCNTs* c) ZrO_2 and d) bare GCE in pH 7 containing 25 µM of p-nitrophenol at scan rate 50 mV/s. B) LSV of *f*MWCNTs/ZrO_2nanocomposite modified electrode for the different concentrations of p-NP (Lab Sample) in pH 7 Inset shows a current vs. Concentration plot of p-NP.

In the next step, linear sweep voltammetry (LSV) has been employed for the selective detection of p-NP. Fig.6B shows the LSV curves of p- NP for various concentrations on *f*MWCNTs/ZrO_2 nanocomposite modified electrode at 50 mV/s. Here the reduction peak current occurs at the potential range of -0.65 V corresponding to redution of p- NP. Further the reduction peak currents of p- NP increases linearly in conjunction with increasing concentrations in the range of 2 to 26 µM. This results validates that the *f*MWCNTs /ZrO_2 nanocomposite film modified GCE possess the specific electrocatalytic activity towards p- NP, which could be considered as the main reason for the successful detection. Based on the calibration plot, the linear regression equation for p-nitrophenol has been expressed as I (µA) = 0.8527 C (µM) + 12.796 , R^2 = 0.9902. The linear response shows the stability and promising electrocatalytic application of the proposed film.The CV and LSV results indicates that the fabricated *f*MWCNTs/ZrO_2 nanocomposite film modified GCE possess the capability for the voltammetric determination of p-NP without any fouling effect. Moreover, a comparison of analytical parameters of *f*MWCNTs/ZrO_2 nanocomposite modified GCE with other mediated p-nitrophenol sensors has been made and given in Table 1.

Table 1

Comparison chart for the electrochemical detection of p-nitro phenol in various other modified electrodes based literature reports.

Modification Method	Detection Limit (µM)	Linear range (µM)	Correlation Coefficient	Stability	Reference
[a]Nano gold/GCE	8	10 to 1000	–	95% (7 days)	26
Poly(propyleneimine)–gold/GCE	0.45	0.61 to 625	0.9994	–	27
Nano porous gold	–	0.25 to 10 mg dm^{-3}	0.9941	–	28
[b]MWCNT/GCE	0.4	2–4000	0.9965	–	29
Nano-Cu_2O/Pt electrode	0.1	10–1000	0.9985	–	30
Silver particles/GCE	0.5	1.5–140	0.9800	–	31
[c]*f*MWCNTs/ZrO_2/GCE	**0.03**	**2 to 26**	**0.9902**	**98% (7 days)**	This Work

[a]GCE – Glassy carbon electrode

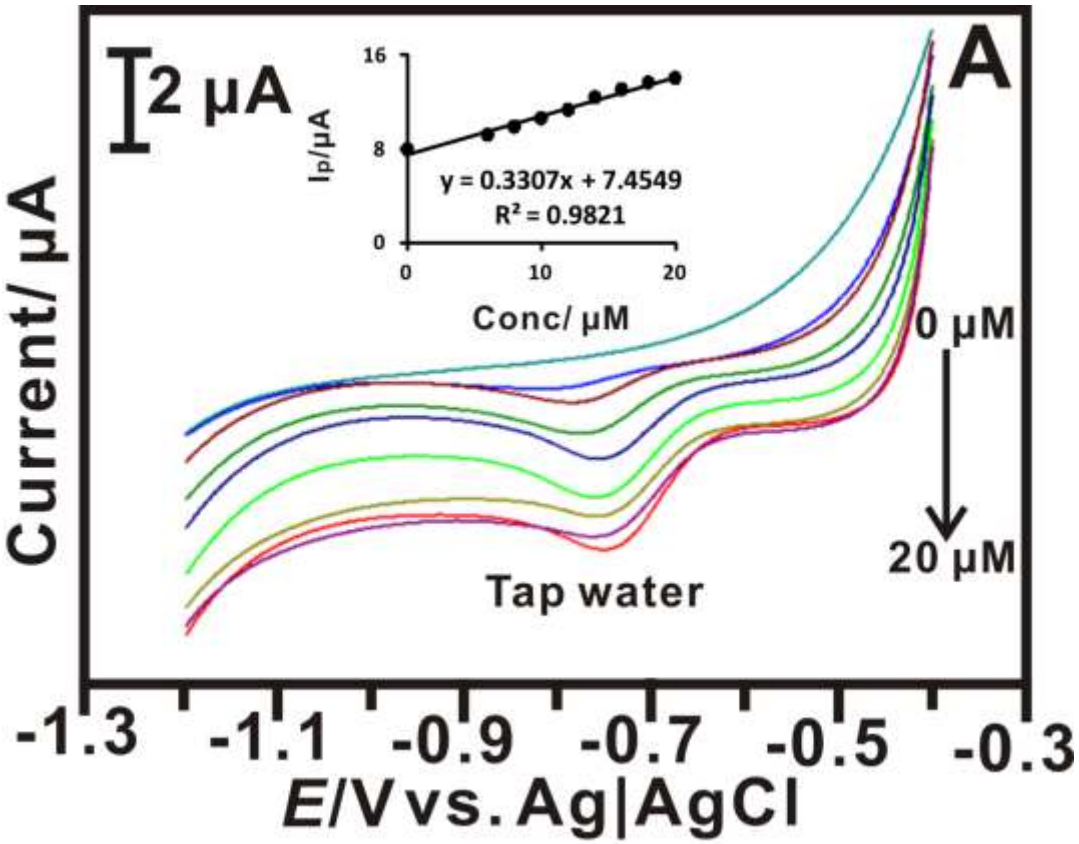
[b]MWCNT/GCE – Multi walled carbon nano tube.

[c]*f*MWCNTs – Functionalized Multi walled carbon nano tube

3.6 Determination of p-nitrophenol for different water samples

The practical performance of the *f*MWCNTs/ZrO_2 nanocomposite film modified GCE has been employed for the detection of p-NP in water samples. The river water collected from near area and tap water was collected from laboratory tap, which are utilized for the real sample analysis.

Beginning of the the real sample analysis, freshly collected water samples (pH 6.7) were filtered several times using Whatman filter paper (grade 1). Filtered water samples were used for the further experiments. Fig.7A shows the LSV of p-NP analysis from tap water using *f*MWCNTs/ZrO_2 nanocomposite modified GCE at scan rate of 50 mV/s. Each addition of tap water sample cantaining various concentration (0 to 20 µM) of p-NP, the redution peak increses gradually.Similarly the addition of river water samples (0 to 16 µM) for the detection of p-NP has been displayed in Fig7B. The current versus concentration plot of p- nitrophenol in water samples indicated in inset (7A & B). The linear range dependence of LSV response on concentration of p-NP in tap water is expressed as I (µA) = 0.330 C (µM) +7.454, R^2 = 0.982 and for river water has been found as I (µA) = 0.152 (µM) +8.510, R^2 = 0.977). Based on these results, it clearly validates that the fabricated GCE has capability for the detection of p-nitrophenol in real samples.



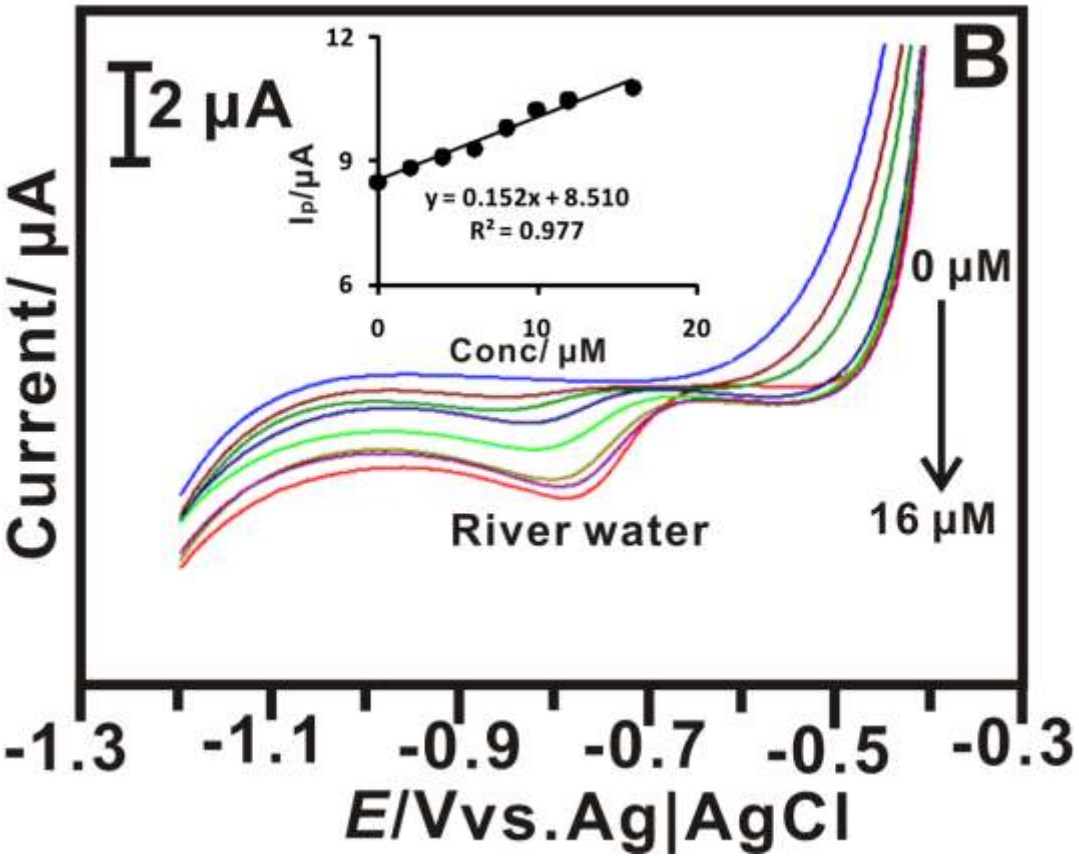


Fig.7. LSV obtained at *f*MWCNTs/ZrO_2/GCE for detection of p-nitrophenol A) tap water B) river water (Inset Shows current vs. Concentration plot of p – nitrophenol (Real Sample) (a) Tap water and (b) River water.)

3.7 Repeatability, reproducibility and Stability studies

The repeatability of the *f*MWCNTs/ZrO_2 composite modified film for the detection of p-NP has been evaluated by using LSV studies. LSV was recorded in pH 7 PBS at the scan rate of 100 mV/s in the presence of p-NP at 20 µM respectively. The fabricated GCE for p- NP sensors shows the good repeatability with a relative standard deviation (RSD) value of 4.5 % (n = 10) . Moreover, it exhibits a good reproducibility with an and RSD value of found as 3.5% for 5 successive individual measurements. The repeatability and the reproducibility values confirmed that the fabricated film was suitable for the detection p-NP. Further the stability of the film has been examined by storing it at the room temperature in the open air condition (Fig.8). After 10 days , it showed a stable behaviour only with a gradual decrease (5 %) from the initial current values. These results authenticating that, the modified electrode has the good repeatability and reproducibility for the detection of p-NP.

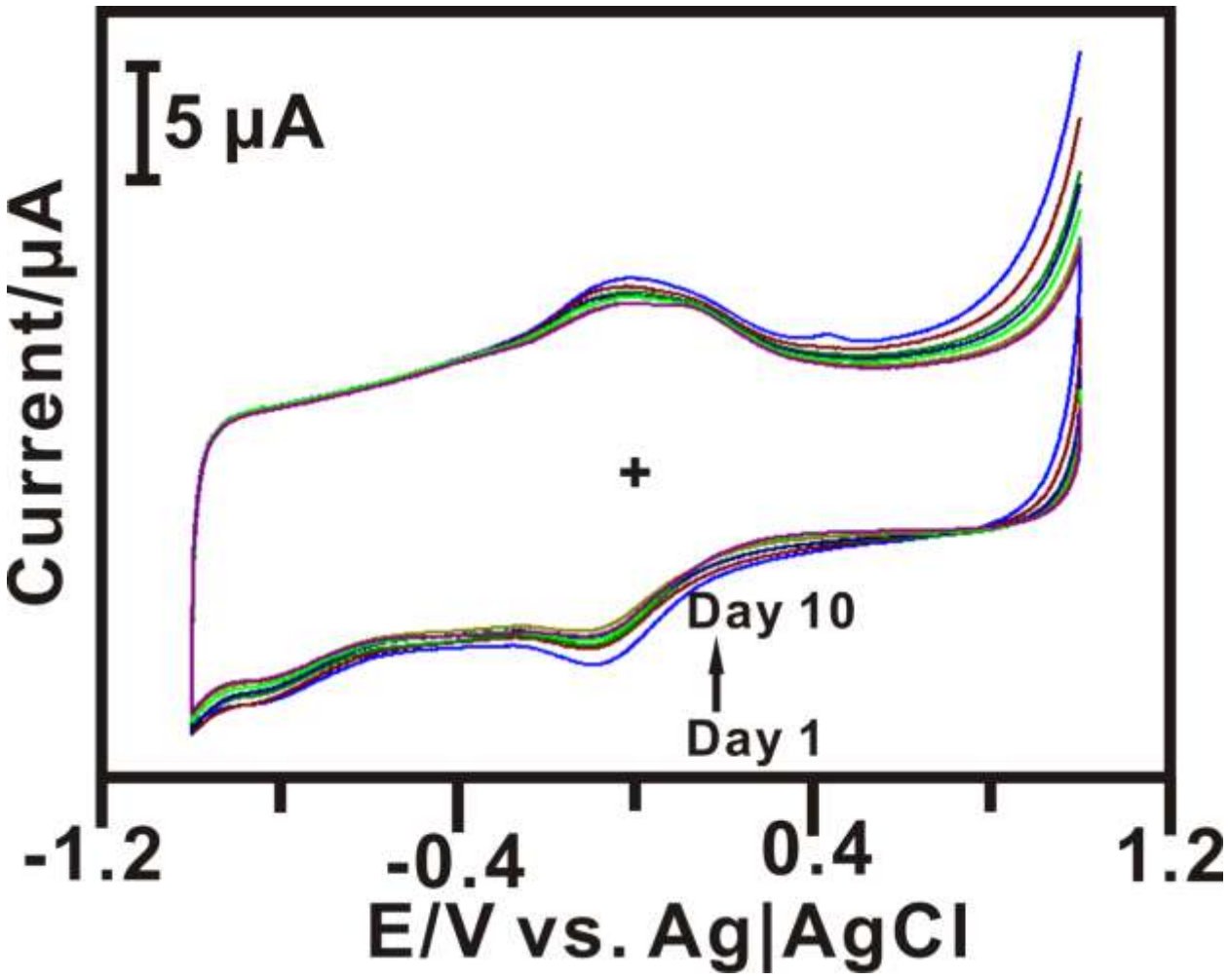


Fig.8. CV response of *f*MWCNTs/ZrO_2 nanocomposite film modified GCE in the pH 7 PBS for 10 days (a-g).

4. Conclusions

In conclusion, we have successfully fabricated a *f*MWCNTs/ZrO_2 nanocomposite film by a simple electrodeposition method. Fabricated nanocomposite film was characterized by FESEM analysis. This Result shows that , as prepared ZrO_2 nanoparticles were strongly incorporated on the *f*MWCNTs GCE. The electrochemical activities of the *f*MWCNTs//ZrO_2 nanocomposite film have been examined using CV and EIS analysis. The nanocomposite modified GCE possess the

high electro active surface area, which has well suited for the voltammetric detection of p-nitrophenol. The proposed *f*MWCNTs//ZrO_2 nanocomposite modified GCEs remarkably suppressed the interference effect and showed well defined reduction peaks for the determination p-nitrophenol. Finally, the *f*MWCNTs/ZrO_2 nanocomposite modified GCE have capability to detection of p- nitrophenol in tap and river water samples.

Acknowlegement

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