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Short Communication

Electrochemical Behaviour of Silver Nanoparticle-MWCNTs Hybrid Nanostructures Synthesized via a Simple Method

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As the synthesis via completely green method is emerging, determination of the electrochemistry properties of the as-synthesized nanomaterials has become an important aspect of research. We herein investigate for the first time the inherent electrochemistry of silver nanoparticle modified multiwall carbon nanotubes (Ag NPs-MWCNTs) hybrid nanocomposites that was synthesized via a simple method using cyclic voltammetry (CV) as a diagnostic technique. The result obtained was compared with multiwall carbon nanotubes (MWCNTs), acid functionalized MWCNTs (MWCNT-COOH) and as-synthesized silver nanoparticle (Ag NPs) modified on the glassy carbon electrode (GCE). A detailed analysis of the cyclic voltammograms gave fundamental electrochemical parameters including the transfer coefficient (α) and the diffusion coefficient (D). The transfer coefficient for the Ag NPs-MWCNTs/GCE was found to be greater than that of MWCNTs/GCE while the diffusion coefficient of Ag-NPs-MWCNTs/GCE was calculated to be 5.11 $\times 10^{-5}$ cm^2 s^{-1} which is higher than both pristine MWCNTs/GCE and MWCNT-COOH/GCE.

Keywords: Ag-MWCNT, green synthesis, electrochemical behavior

1. INTRODUCTION

Electrochemical methods are considered to be more advantageous in characterisation than the conventional methods like spectrophotometric techniques, fluorimetric techniques etc because of their quick response, high accuracy and wide range of detection [1, 2]. Modification of standard gadgets and devices using multifunctional materials in order to inculcate novel properties has become a common practice. Nanomaterials like metal nanoparticles, carbon nanotubes (CNTs), nanosilicates etc. and other surfactants are now commonly used for this kind of modifications [3-5]. In order to improve the selectivity and reproducibility of electrodes used for the electrochemical analysis, modifications using various nanomaterials have been reported [6-8]. Carbon nanotubes (CNTs) are among the most studied nanostructured materials useful for the modification of electrode surfaces because of their high electrical conductivity, high surface area, significant mechanical strength and good chemical stability [9, 10]. CNTs can act as an electron mediator which helps in lowering the overpotential required for electrochemical oxidation of the analyte and enhance the sensitivity and selectivity of the sensor. Due to its small size and excellent electrical properties, CNTs have also found extensive use as analytical tools, in the construction of devices and sensors [11-13].

Multi-walled carbon nanotubes (MWCNTs) have been used to modify the electrode surfaces in order to increase its sensitivity towards the electrochemical detection of various drugs and enzymes [14, 15]. However, the insolubility of CNTs in almost all solvents makes their manipulation rather difficult, and thereby restricting its use in various electrochemical analyses. In order to improve the solubility of CNTs, various methods like surface functionalization and introduction of structural defects have been successfully carried out [16]. The structural and morphological peculiarities of MWCNTs allow them to serve as a template for preparing metal nanoparticle-MWCNTs nanohybrids [17-18]. Studies have shown that the presence of small amount of metal catalysts in the MWCNTs structures can enhance the electrocatalytic activity of a system [19-20]. Recently there have been some studies on the fabrication of metal nanoparticles decorated CNTs in order to integrate the properties of the two components, as well as measuring their unique electrical, magnetic, catalytic and optical properties [21-23]. Among them, Ag nanoparticles (Ag NPs) attached onto CNTs (Ag NPs-MWCNTs) have gained significant attention due to their potential applications [24-25]. However, little is known about the electrochemistry of these hybrid nanocomposites. In addition, most of these metal NPs before incorporation in to the CNTs are usually prepared using reducing agents that are usually associated with biological hazards to health and environment [26-28]. Since new completely green method of synthesizing metal NPs are emerging, the electrochemistry of these metal hybrid nanostructures in which the metal NPs are produced via completely green method need to be investigated. This will serve as a platform for the production of improved electrochemical sensor with lower overpotential required for electrochemical oxidation of various analytes and enhance sensitivity and selectivity for environmental pollutants. In addition, such hybrid nanostructure will reduce the overvoltage and overcome the slow kinetics of many electrode processes. Thus, in this communication, we report the electrochemical behavior of silver nanoparticle modified MWCNTs hybrid nanostructure. The Ag-NPs were prepared via a completely green method using biocompatible and biodegradable material as both reducing and capping agents before incorporation into the functionalized MWCNTs (F-MWCNTs) while the traditional method of immobilization of the hybrid nanostructure on the surface of the electrodes was used for the immobilization. To the best of our knowledge, no electrochemical study involving silver functionalized MWCNTs synthesized via a completely green method has been reported. The electrochemical behaviour of bare MWCNTs, MWCNT-COOH and Ag NPs was also investigated and compared with Ag NPs-MWCNTs hybrid nanostructures. Since the Ag NPs has been shown to possess high sensitivity, lower detection time and high detection limit for environmental pollutant [29], this report will lead to the fabrication of electrochemical sensors that are simple, cost effective with high sensitivity, lower detection time and high detection limit for remedial /control processes of environmental pollutants.

2. MATERIALS AND METHODS

2.1. Materials

All the chemicals were of analytical grade and used as purchased without any further purification. MWCNTs were purchased from Nanoshell, Chennai, India. $AgNO_3$ was purchased from Alba cheme, while gelatin, dextrose, sulphuric acid, nitric acid and hydrochloric acid were from Merck SA. All glasswares used in the experiments were cleaned and washed thoroughly with double distilled water and dried before use.

2.2. Preparation of silver decorated MWCNTs nanocomposites

In order to improve the solubility of MWCNTs, it was initially functionalized with acid group. MWCNTs were first treated with a 3:1 mixture of 40 mL concentrated sulfuric and nitric acid to form an acid functional group on the MWCNTs surface. The prepared functionalised (F-MWCNTs) were then dried in vacuum at 40 $^{\circ}$C overnight. In order to introduce Ag NPs to the F-MWCNT surface, the material was treated with gelatin capped silver nanoparticles which were synthesized using our previous reported procedure [29]. After some time, the solution was filtered to obtain Ag-NPs-MWCNTs which were then dried for characterization.

2.3. Characterization

FTIR spectra of the Ag NPs-MWCNTs were recorded with Nicolet-Nexus 670. A JEOL JEM-3010 electron microscope operating at 200 kV was used for the TEM measurements of the silver decorated MWCNTs. For the TEM measurements, samples were prepared by drop casting the solution on a copper grid and dried under ambient conditions. Electrochemical experiments were performed with an electrochemical work station Autolab PGSTAT 101 coupled with a conventional three-electrode system. All electrochemical experiments were carried out in 1 M H_2SO_4 solution, purged with high purity nitrogen gas and blanketed with nitrogen atmosphere during measurements. The solutions were prepared from analytical grade reagents and, water distilled and purified in a Millipore system. Glassy carbon electrode (GCE) was used as the working electrode ($A = 0.071$ cm^2), a platinum wire electrode and Ag/AgCl (3 M NaCl) electrodes from Metrohm SA were used as auxiliary and reference electrodes respectively.

Prior to modification, the GCE was pretreated to mirror-like using the following protocol. The glassy carbon electrode was polished repeatedly with 1, 0.3 and 0.05 μm alumina slurries in sequence and sonicated in water and ethanol, successively for 10 min. 5 mg Ag NPs-MWCNTs were dispersed in 5 mL H_2O under continuous stirring for 5 min. 20 µL of the dispersed Ag-NPs-MWCNTs was drop coated on the surface of the pretreated GCE and dried. For comparison, the modified GCE was also prepared using MWCNT, MWCNT-COOH and Ag-NPs. All potentials were quoted with respect to Ag/AgCl. The experiments were carried out at room temperature (25 °C). Using the modified GCE as working electrode, the cyclic voltammograms (CV) were recorded in the potential range of -1.5 to +1.6 V with the scan rate of 100 mV/s. In order to study the influence of scan rates on the electrochemical behavior of the various modified GCE, different scan rates at 25, 50, 75, 100, 125 and 150 mV/s were used.

3. RESULTS AND DISCUSSION

MWCNTs surface without any functional group are rather inactive and it is very difficult to disperse them in solvents. In order to enhance the surface activity and improve its dispersability, various surface functionalization methodologies were adopted. In this study, acid functionalization of MWCNTs was carried out. The FTIR spectrum of the MWCNT-COOH given in Fig. 1A confirms the acid functionalization of the MWCNTs surface. The MWCNT-COOH spectrum shows peaks at 1706 cm^{-1} and 1260 cm^{-1} which were characteristic absorption peaks for C=O and C–O stretching bands of carboxylic acid group [30].

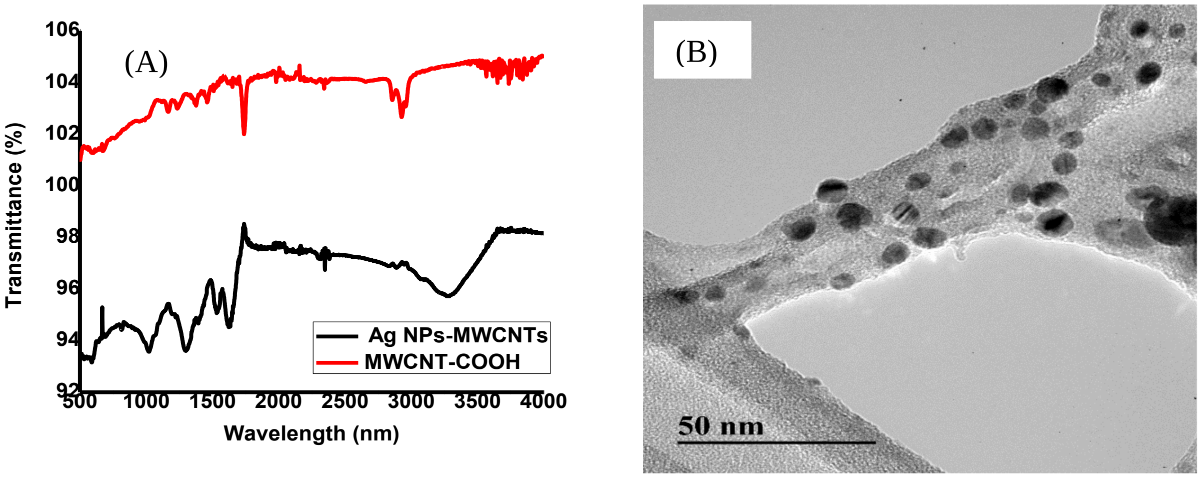

Figure 1 (A) FTIR spectrum of MWCNT-COOH and Ag NPs-MWCNTs (B) TEM image of Ag NPs-MWCNTs

A broad absorption peak was observed between 3300 ~ 3500cm^{-1} which indicate the presence of free hydroxyl group (-OH) which again confirms the acid functionalization of the MWCNTs. After the addition of F-MWCNTs to the gelatin capped AgNPs, the AgNPs interact with F-MWCNTs through the $-NH_2$ group present in the gelatin to form a covalent bond with the carboxyl group of the F-MWCNTs. The FTIR spectrum of the AgNPs-MWCNTs (Fig. 1) clearly shows the covalent bond formed between MWCNT-COOH and silver nanoparticles. A broad peak between 2965-3664 cm^{-1}

shows the presence of –CO-NH- bond formed between the amine group of gelatin capped Ag NPs and carboxyl group of F-MWCNTs thus confirming the formation of Ag NPs-MWCNTs hybrid nanocomposite. The amide linkage was further confirmed by the peaks at 1549 cm^{-1} which is due to the –NH bend. The TEM image of the Ag NPs-MWCNTs in Fig. 1B clearly shows the presence of Ag NPs homogenously dispersed on the surface of the MWCNTs with no agglomeration. The particle size ranges between 7-12 nm with an average particle diameter of 9.68 ± 1.44 nm. The diameter and aspect ratio of the F-MWCNTs was about 32.9 ± 1.37 nm and 6 nm respectively.

Fig. 2 shows the cyclic voltammograms of modified GCE at a scan rate of 0.05 V/s within a potential window of -1.8 to +1 V. For pristine MWCNTs/GCE an oxidation peak was observed at 0.7 V with no significant reduction peak during the reverse cycle. The acid functionalized (MWCNT-COOH/GCE) has a cathodic peak around +0.001 V. The hydrogen from the carboxylic group is responsible for the reduction reaction of MWCNT-COOH.

After functionalizing the MWCNTs with Ag NPs, the hybrid Ag NPs-MWCNTs/GCE showed characteristic peaks observed in the Ag NPs voltammogram thus confirming the effective functionalization of the F-MWCNTs. Furthermore, the reduction current of MWCNTs/GCE increased significantly after functionalization. This shows that the Ag NPs on the surface of MWCNTs is initiating the electron movements on the carbon nanotube surface.

The Ag NPs/GCE and Ag NPs-MWCNTs/GCE CV has only one small anodic peak around +0.06 V and four cathodic peaks at +0.5, -0.07, -1.0 and -1.5 V. The cathodic peak at -0.07 V is ascribed to the presence of COOH, while the other three peaks which are only present in Ag NPs containing compounds may be due to the presence of capping agents on the surface of the nanoparticle.

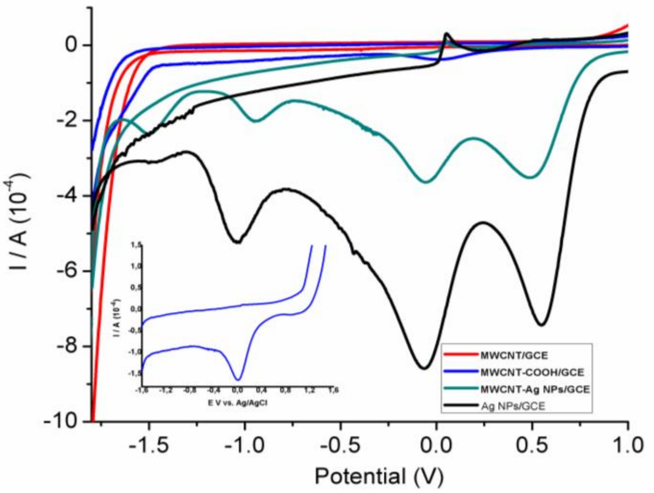

Figure 2 Cyclic voltammograms of the hybrids films (presence and absence of Ag NPs) on GCE; in 1M HCl at 50 mV/s scan rates. Insert: MWCNT-COOH

Gelatin, which is the capping agent for silver used in this study is a complex mixture of amino acids, therefore their amine /amides groups can be reduced at different potential due to their varying chemical environment. The smaller size of the anodic peak and the absence of the characteristic Ag^0

/Ag^+ redox couple strongly suggest that the Ag-NPs in the hybrid is bound to the gelatin /MWCNT. Thus collaborating the TEM microgram (Fig. 1B) depicted above.

The influence of the scan rates on the electrochemical behavior of all the samples studied (MWCNTs/GCE, MWCNT-COOH/GCE, Ag NPs/GCE, and Ag NPs-MWCNTs/GCE) is depicted in Fig. 3 (A to D). All the CVs were characterized by an increase in current with increasing scan rate. However, for all Ag NPs containing materials (Ag NPs/GCE, MWCNT-Ag NPs/GCE) the current increase was accompanied by a marked shift in potential as well as additional peaks being observed as the scan rate increases. The notable changes in the Ag NPs voltammograms (Fig. 3C) is the anodic peak broadening, peak splitting as well as additional cathodic peak appearance at -0.07 V as the scan rates is increased. These changes are due to electrochemical dissolution (stripping) of silver nanoparticles on the electrode surface, at ~ +0.06 V and reduction of the generated silver ions in the oxidative part of cycle from the solution at ~ -0.07 V. The change in appearance of the anodic peak as the scan rates increases possibly indicates the presence of various forms of Ag NPs-gelatin hybrids or possible degradation of the nanoparticles. However, these changes were not observed in the Ag NPs-MWCNTs hybrid (Fig. 3D) suggest some stability of the compound in the presence of MWCNTs.

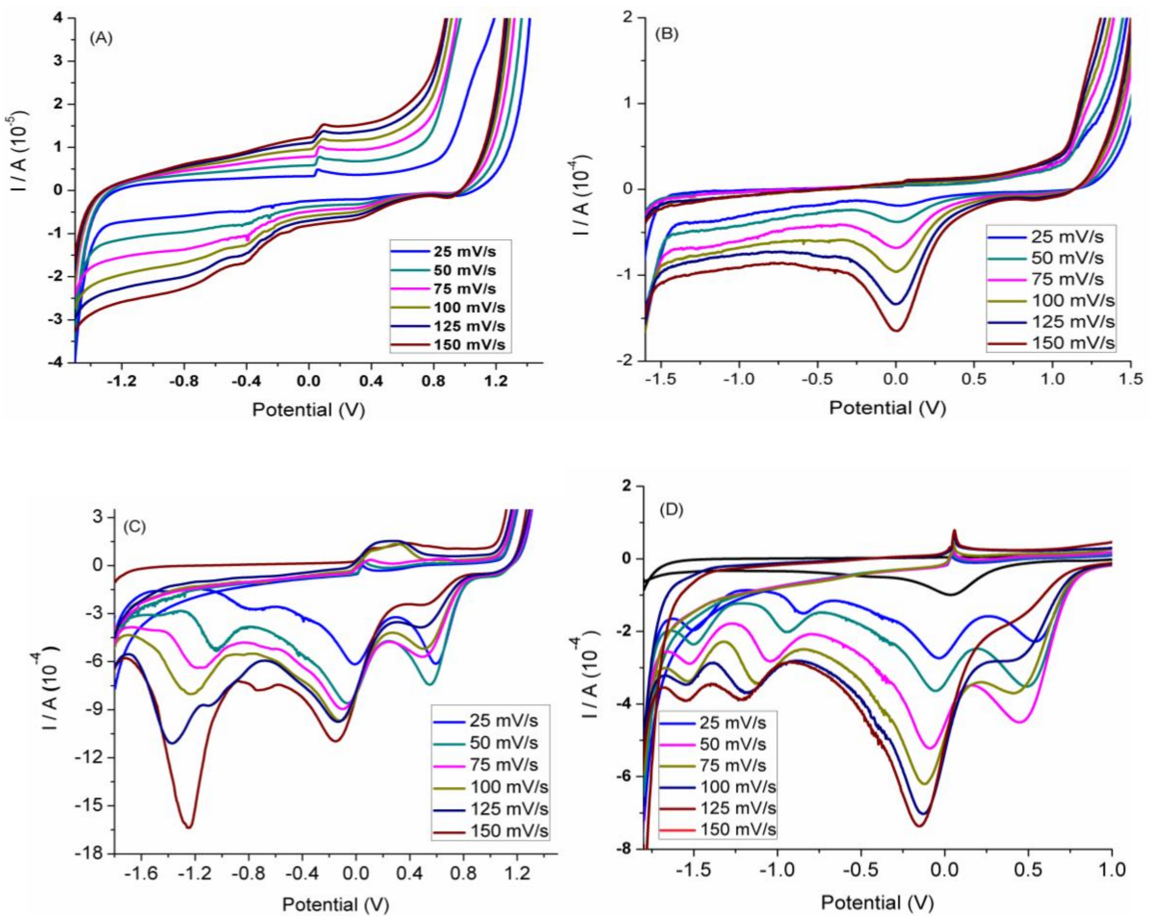

Figure 3. Cyclic voltammogram of the hybrids at various scan rates: (A) MWCNT/GCE (B) MWCNT-COOH/GCE (C) Ag NPs/GCE and (D) MWCNT-Ag NPs/GCE

From the cyclic voltammograms of modified GCE surfaces at various scan rates, the relationships of the redox peak potentials with the scan rate were applied to calculate the electrochemical parameters such as charge transfer coefficient (α) using the following Laviron's equations [31].

$$\log ks = \alpha \log(1-\alpha) + (1-\alpha)\log\alpha - \log\left(\frac{RT}{nF}\right) - (1-\alpha)\alpha nF\,\frac{\Delta E_p}{2.3RT} \quad (1)$$

$$I_p = \left(\frac{n^2F^2}{4RT}\right)\Gamma AV \quad (2)$$

$$\Gamma = Q/nFA \quad (3)$$

Graph from equation 2 and Randles-Sevcik's plots are shown in Fig. 4 (A) and (B) respectively. From these figures there is a mark reaction difference in the presence and absence of Ag-NPs. Randle plots are linear in the absence of Ag-NPs while the Equation 2 plots are linear in the presence of Ag-NPs. This indicates that the characteristic redox peak of silver at around 0.6 V was shifting as the scan rate increased in all Ag-NPs containing hybrids. From the graphs in Fig. 4, there exist a mixture of both adsorption and diffusion occurring at the electrode surface. The predominant process depends on the scan rate.

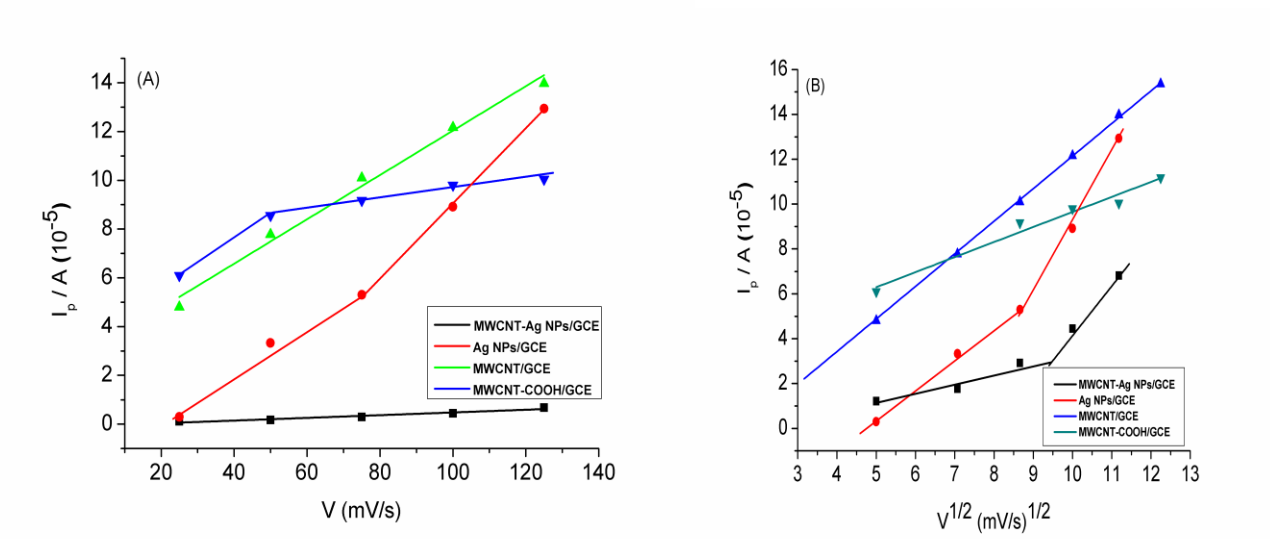

Figure 4. Equation 2 (A) and Randles-Sevcik's (B) plots of MWCNT, MWCNT-COOH, Ag NPs and MWCNT-Ag NPs deposited on GCE

The electrochemical parameters of all the systems are in Table 1. The diffusion coefficient value increases from 5.11× 10^{-6} to 5.06 × 10^{-5} after the functionalization of the F-MWCNTs surface with Ag NPs. This clearly shows that the conductivity of the hybrid structure is higher than the F-MWCNTs. Furthermore, from the slope of the linear plot of I_p versus V, the surface coverage of the electrode (Γ) was determined using equation (2), where Γ is the surface coverage in mol/cm^2, Q is the charge in coulombs, A is the area of the electrode surface in cm^2, and n is the number of electrons transferred during redox transformation.

Table 1. Electrochemical parameters obtained from Equation 2 and Randles-Sevcik's plots

	MWCNT/GCE	MWCNT-COOH/GCE	MWCNTs-Ag NPs/GCE	Ag NPs/GCE
α	0.7	0.1	0.8	0.5
ΔE (1^{st} scan) (V)	-	-	-0.191	-0.194
D (10^{-5} cm^2/s)	0.51	2.06	5.06	6.03
Band gap (eV)	-	-	2.68	2.67
Γ (10^{-11} $molcm^{-2}$)	0.570	2.289	3.48	7.732
Charge (10^{-8} C)	0.935	3.754	5.710	12.680
E^0	-	-	0.204	0.231
Charge transfer (α)	-	-	2.759	2.995
Randles plot (R^2)	0.9989	0.9638	0.8417	0.9384
Equation 2 plot (R^2)	0.9874	0.7767	0.9243	0.9870

The surface concentration of the electroactive species was estimated as shown (Table 1) according to equation (2) using anodic peak as similarly discussed [32]. Other values also show the dominance of Ag-NPs properties. From these data, the electrochemical properties of the Ag-NPs-F-MWCNTs are better than those of the F-MWCNTs.

4. CONCLUSION

The electrochemical behavior of silver modified multiwall carbon nanotube (Ag-NPs-MWCNTs) hybrid nanostructure modified GCE was investigated. The Ag-NPs were prepared using completely green materials followed by dispersion in F-MWCNTs. The transfer coefficient (α) and diffusion coefficient (D) calculated from CV responses were higher for Ag NPs-MWCNTs/GCE compare with MWCNTs/GCE and Ag-NPs/GCE. The diffusion coefficient of MWCNT-COOH/GCE was highest but the transfer coefficient was low. The study showed that functionalizing MWCNTs surface with Ag-NPs indeed improves its conductivity which will widen the application of these materials as optical materials and sensors. Since the Ag-NPs has been shown to possess high sensitivity, lower detection time and high detection limit for environmental pollutant, therefore this data reported will lead to the fabrication of electrochemical sensors that are simple, cost effective with high sensitivity, lower detection time and high detection limit for remedial /control processes of environmental pollutants.

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