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Chemically modified multiwalled carbon nanotube carbon paste electrode for copper determination

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Abstract:

A new Cu^{2+} carbon paste electrode based on incorporation of new (CPE) via chemically modified multiwalled carbon nanotube (CMMWCNT) on the graphite matrices has been constructed. Surface of MWCNT was modified by performing a couple reactions between trimethoxysilylpropylethylendiamine (TMSPEDA) and 2-hydroxybenzaldehyde (2-HBA). This new material was characterized with different techniques such as FT-IR, SEM and BET analysis. The influence of variables including sodium tetraphenylborate (NaTPB), graphite powder, Nujol, amount of (MWCNT-SPAEIMP) and Ag nano particles loaded on AC on the electrode response was studied and optimized. At optimum values of variables set as carbon powder, carrier, NaTPB and nujol, the response of Cu^{2+} selective electrodes in the absence and presence of Ag-NP-AC was linear in concentration range of 5.0×10^{-6} - 1.0×10^{-1} and 5.0×10^{-7} - 1.0×10^{-1} mol L^{-1} with slope 29.93 and 29.11 mV with detection limit of 3.2×10^{-6} and 2.5×10^{-7} . The good performance of electrode viz. reasonable wide pH range (2.0-5.5), fast response time (<15 s) and adequate life time (2 months) in addition to low RSD (<4%) show the utility of the proposed electrodes for Cu^{2+} ion content quantification in various situations. The moderate selectivity coefficient evaluated by separation solution method (SSM) and fixed interference method (FIM) indicates efficiently the discriminating ability of proposed electrode for copper ion evaluation.

Keyword: Carbon Paste Electrode, chemically modified multiwalled carbon nanotube, Copper Ion, Ag nano particle, Potentiometric Sensors.

1. Introduction:

The research on fabrication of new ion sensors has caused a fundamental development in potentiometry over the past few decades [1]. Ion selective electrodes (ISEs) are well known and efficient tools for accurate and repeatable determination of various target molecules or ions in biological and industrial analysis. In view of distinct advantage of ISEs huge amount of efforts have been devoted to make selective sensors for different ions [2].

In addition to conventionally constructed electrode, the carbon paste type electrode has become attracted and wide application for potentiometric determination of target species. The development and application of potentiometric sensors is extensively concern to the usage of selective recognition elements (ionophore). Among various classification of mechanism of ISEs response, carrier-based ion-selective electrode (ISEs) on the basis of chemical recognition principles has the best characteristic performances [3]. One of the most prominent problems in ISEs is the leaching of ionophore to the bulk sample solution that strongly is forbidden by application of chemically modified ionophore. Carbon pastes electrodes (chemically modified carbon paste electrodes (CMCPEs)), fabricated in simple way. CMCPEs based on modification of MWCNT surface due to enhance in charge transfer and the number of surface reactive atom and surface area lead to improvement in electrochemical response. In such electrodes, a stable electrochemical response can be obtained following renew of electrode surface by removing an outer layer of the paste and re-smoothing the electrode surface.

Copper contents have great importance and diverse role in various biological, human life and industrial activities. Long-term exposure of human to copper ion causes irritation of the nose, mouth and eyes in addition to headache problems [4-7]. Because of this widespread appearance and application and high amount of tolerable copper content (2 mg L^{-1}), its determination has great importance. Its excessive intake manifests in certain human diseases

such as Menke's syndrome and Wilson's disease. Therefore, Cu^{2+} ion determination is important in term of its utility and toxicity. Different analytical methods are being used for determination of Cu^{2+} ion [8-12]. Application of ion-selective electrodes (ISEs) makes possible accurate, rapid, non-destructive and low cost, fast response and convenient analysis with easy handling and any sample pretreatment [13-18].

In recent years, great attention has been devoted to the application of nano-structure materials, especially carbon nanotubes (CNTs). In particular, there have been an increasing number of applications of CNTs in several chemical analysis fields [19-22]. The combination of specific metal-ligand interaction and addition of carbon nanotubes (CNTs) is the most important recognition mechanism [23-30] facilitates the electron transfer between the electro-active species and the electrodes.

Generally, chemically modified electrodes (CMEs) [30-36] formed by covalent binding of mono or multi layers of molecules on the electrode surface. Low selectivity and efficiency of untreated or oxidized-multiwalled carbon nanotubes (MWCNT) may be concern to the presence of $-\text{NH}_2$ and $-\text{COOH}$ [37-38]. The change in nature of surface by suitable materials generally improves selectivity and sensitivity of the determinations [39-41]. The most selective interaction trend for preparation of copper selective electrodes is based on application of chemical recognition elements (organic or inorganic hydrophobic chelating agent) with selective tendency for binding of Cu^{2+} ion [15-18] [33-34] [42-47]. Most of the previously reported electrodes in view of their advantage suffer from limitations such as low linear range, high detection limit and response time (Table 1). In our sense, these limitations can be overcome by simultaneous incorporation of nanoparticles and chemical immobilization of carbon surface.

The introduction of nanostructured material enables the development of new potentiometric sensors via replacing the polymeric membrane with the transducers. The functionalization of

carbon nanotubes makes possible the direct linkage of the receptor molecules as alternative pathway instead of entrapping improve the electrode performances. These types of sensors are very different from ISEs in term of : (1) the receptor is immobilized onto the walls of carbon nanotubes instead of being entrapped in a polymeric membrane; (2) the receptor is in direct contact with the target, and the recognition event is based on an affinity process; (3) the targets are not necessarily small ions, but instead can be large multiunit species such as proteins or complex systems such as microorganisms; (4) the sensing mechanism is based on a superficial phenomenon, very different from the well-established phase-boundary potential model in ISEs; (5) the sensing mechanism is based on the potential generated by the different charged species in the chemical environment of the nanotubes, which in turn means that the calibration curves do not follow the classical Nernstian model; (6) the sensitivity of the new sensors is very low compared with that of ISEs, but it is high enough to enable the detection of the target [66].

In progress of other our attempts, new copper selective electrodes based on synthesis of CMMWCNT was applied for design of Cu^{2+} ion carbon paste electrodes. In this paper, MWCNT-SPAEIMP (product of reaction between trimethoxysilylpropylethilendiamine (TMSPEDA) and 2-hydroxybenzaldehyde (2-HBA)) was chemically bonded to MWCNTs to produce a new material (MWCNT-SPAEIMP) for preparation of new Cu^{2+} ion selective electrode.

2. Experimental Detail

2.1. Apparatus, reagents and materials

Analytical-reagent grade ethanol and methanol were supplied from Fluka (Buchs, Switzerland). All the potential and pH measurements were carried out with a pH/Ion meters model 780 (Metrohm Co., Herisau, Switzerland). All chemicals used were of analytical reagent grade and doubly distilled water was used throughout. Graphite powder and high

purity Nujol oil from Fluka (Buchs, Switzerland) used for the preparation of the modified carbon paste electrode. The stock solution of 0.5 M Cu^{2+} ion was prepared by dissolving appropriate amount of nitrate salt form Merck (Darmstadt, Germany) in 100 mL doubly distilled water. MWCNT with the highest purity available are purchased from Merck (Darmstadt, Germany) was used. The ionophore MWCNT-SPIMP (Fig. 1), were synthesized in our laboratory. Typical procedure for synthesis of ionophore is explained in Section 2.2.

2.2. Synthesis of chemically modified MWCNT with 2-((3silylpropylaminoethylimino) methyl) phenol (MWCNT-SPAEIMP)

The (CMMWCNT) were prepared according to our previous reports in three stages including activation of MWCNT, supporting of organic spacer (trimethoxysilylpropylethylendiamine (TMSPEDA)) and finally generation of Schiff base chelate on it. This work was performed by treatment of 1.0 g of MWCNT with 250 mL of 4M nitric acid under severe stirring for 36 h at room temperature. Then the mixture was filtered and washed several time with double distilled water and dried for 1 day at room temperature. The Schiff base chelate generation on surface was carried out by addition of 2.2272g of 2-hydroxybenzaldehyde (2-HBA) to suspension of previous obtained solid in methanol (25 mL) and then reflux of the reaction mixture for 24 h. In final, *CMMWCNT* greenish black solid entitled as MWCNT-SPAEIMP was filtered and washed three times with methanol and dried at room temperature. The schematic diagram of ionophore preparation is presented in Figure 1.

2.3. Synthesis of Ag nanoparticles

The Ag nanoparticles (Ag NPs) were synthesized in a one-step reduction process in an aqueous solution. All reactions were carried out in oxygen free water under nitrogen. Following addition of 400 μL of 0.1 M AgNO_3 into 100 mL of 0.15 w/w% of starch solution,

the mixture was stirred vigorously for 1 h at pH of 8.0. In these conditions, the initial reaction mixture was colorless and the growth of the Ag NPs was monitored at different intervals using UV–Visible absorption spectroscopy. Formation of turned light yellows following about 1 h show production of the Ag NPs and after keeping at 50 °C for 24 h the reaction color became yellow. In the next step, 10 g AC was added to the mixture in a 250 mL flask and stirred for up to 12 h. This treatment led to deposition of the Ag NPs on the activated carbon (Ag NPs-AC). The Ag NPs-AC were then filtered and extensively washed with double distilled water. A mortar was used to homogeneously ground the Ag NPs-AC powders. The Ag NPs-AC was stored in air at room temperature and was found to have a shelf life of at least 1 year.

2.4. Electrode preparation and potential measurements

Carbon paste was prepared by hand mixing of 50 mg of reagent-grade graphite powder and 100 mg CMMWCNT, 5ml THF and 18 mg of Nujol oil with a mortar and pestle. Modified carbon nanotube paste electrodes were prepared by hand mixing different amount Ag nano particle with 50 mg of reagent-grade graphite powder and 36 mg of Nujol oil with 100 mg CMMWCNT and additive (NaTPB) solved into THF to get different compositions. The solvent evaporated by stirring. Both unmodified and modified pastes were packed into the end of polyethylene tube (*ca.* 3.4 mm *i.d.* and 2.0 cm long). Electrical contact was made by inserting a copper wire into the polyethylene tube at the back of the mixture. When necessary, a new surface was obtained by pushing an excess of paste out of the tube and polishing it on a weighing paper.

2.5. Measurements of electromotive force (emf)

All measurements of emf were made at 25°C by a Metrohm pH/Ion meter, model 780 (Metrohm Co., Herisau, Switzerland) with a double junction Ag/AgCl, KCl (saturated) electrode as reference electrode in the cell assembly as follows:

Ag/AgCl || Cu²⁺ ion solution | CPE | Cu wire. Absorbance measurements were carried out with a Jasco model V-570 spectrophotometer (Jasco Co., Hachioji, Tokyo, Japan) and atomic absorption measurements were carried out by use of Varian Spectra AA model 220 (Varian Co., Walnut Creek, CA). ¹H NMR, FT-IR and GC–Mass spectroscopies were, respectively carried out with Bruker 250MHz (Bruker Co., Ettlingen, Germany), Shimadzu FTIR-8300 and Shimadzu GCMS-QP1000EX spectrophotometers (Shimadzu Co., Tokyo, Japan).

2.6. Pretreatment of real sample

Homogenized real sample 20 g was weighted accurately and in a 100 mL beaker was digested in the presence of an oxidizing agent with addition of 10 mL concentrated HNO₃, 3 mL H₂O₂ 30 (w/w %) and 5 mL HClO₄ 70 (w/w %) following heating for 1 h. The content of beaker was filtered through a Whatman No. 40 filter paper and again 5 ml concentrated HNO₃, 3ml H₂O₂ 30 (w/w %) was added and heated until 1 h, then diluted to 500 mL with distilled water. Then its pH was adjusted and the above procedure for determination of copper content was applied. The copper content was evaluated by standard addition method.

3. Result and Discussion

The synthesized CMMWCNT was characterized by FT-IR, SEM and BET as show in Figures 2a-c, 3 and 4. The FT-IR-spectroscopy, SEM and BET data are used to prove chemical modification of the MWCNTs surface. The IR spectrum of activated

MWCNTs(Fig.2a) shows absorption frequencies at 3400-3600 (bw), 1627(s), 1155(s), 673(s), 592(s) cm^{-1} maybe assigned to stretching and bending of OH, C=O, C-O, C=C groups. After supporting the TMSPEDA on activated MWCNT, its IR spectrum (fig. 2b) exhibited some new absorption frequencies such as 2911(w), 2890(w), 1635(w), 910(w), 1553(w), 1031(s), 1098(s) assignable to stretching and/or bending of C-H, N-H and C-N in new added organic moiety to surface confirming its binding. Finally, Schiff base modification of surface to obtain MWCNT-SPAEIMP is proved by the appearance of characteristic absorption frequencies (Fig. 2c) such as 3408(m), 3073(w), 2857(w), 1622(s), 1582(s), 1528(m), 1299(m), 1111(s), 964(m) that may be attributed to O-H, aromatic C-H, iminic C-H, iminic, C=N, benzene ring C=C, C-N, C-O and out of plane bending of O-H respectively. The response feature of the copper CPE such as response time, life time, selectivity and chemical stability depend on ratio of electro-active phase and the binder material [51]. Understanding the chemical and physical processes including the ion fluxes in the sensing layer (contains the ionophore) led to very low limits of detection and increase selectivity. Generally, omitting the inner water solution improved the performance of the electrodes [64-65]. To investigate the influence of amount of carbon paste ingredients on the electrode response, response properties of similar electrodes incorporating various amount of chemically modified MWCNT has been recorded and respective results show that increasing amount of chemically modified MWCNT to 25 mg led to achieve Nernstian potentiometric response and further addition cause decrease in response properties such as linear range and slope (Table 1). These behaviors probably can be related to change in stoichiometry of complexes of metal ions with carrier or surface saturation and in-homogeneity of carbon paste matrices. Generally, addition of lipophilic additive in ion selective electrodes by simultaneous reducing ohmic resistance and increasing the rate and kinetic of mass transfer enhances the response behavior and selectivity of the membrane electrodes. On the other hand, the perm-selectivity optimization

of the membrane sensor is known to be highly dependent on the incorporation of the additional components. It was found by addition of various increment of NaTPB until 10 mg the response properties significantly improved and at higher value due to probable competition of additive with ionophore, linear range and detection limit significantly diminished. Also at lower value, because of low perm-selectivity and higher counter ion fluxes to carbon paste, linear range and slope diminished. In order to improve the response properties of proposed electrode Ag nanoparticle loaded on AC and oxidized MWCNT was impregnated to carbon paste matrices and their response properties in the concentration range of 1×10^{-9} - 1×10^{-1} M was investigated and results are present in Table 2. As it can be seen, addition of Ag-NP-AC to carbon paste matrices (t-test) significantly improve the linear range and detection limit of electrode response that may be attributed to increase in the conductivity of the sensor and the transduction of the chemical signal to electrical. This phenomenon can be explained to the fact that nanomaterials display new properties not shown in the bulk material. Their extremely high surface-to-volume ratio and surface atom promotes a greater interaction with targets as part of the recognition layer. Another probable mechanism is high charge transfer and the extraordinary electrical capacities generated at the interfaces of some nano-structured materials. This behavior has great role and significant when nanomaterials are the transducing components of potentiometric sensors.

The high stability of the recorded potential of electrode based on nanostructured materials is concern to the high double layer capacitance attained from their very large surface to volume ratio. These potentiometric sensors have extremely low limits of detection and significant selectivity coefficients in addition to simplicity, low cost and labelless detection.

The functionalization of nanostructured materials via different sensing layers through various pathway such as covalent and non-covalent bonding and entrapment or encapsulation of the receptors in the nanoparticles [67-71], nanotubes [72-75], nanowires [76-79], and other

nanostructures [80,81] improve the response properties and sensing mechanisms that superior to entrapment of ionophores within the polymeric structure of ion-selective membranes. It was seen that addition of silver nanoparticles to the carbon paste matrices via increasing the tendency of functional group of immobilized MWCNT improve the characteristic performances and figures of merit of proposed electrodes.

3.1. Effect of pH

The influence of pH on the potentiometric response of these new proposed electrodes in the pH range of 1.5 to 6.0 at 1.0×10^{-2} and 1.0×10^{-3} mol L⁻¹ of Cu²⁺ ion solution was investigated and result is shown in Fig. 5. The operational range was studied by changing the pH of the test solution with dilute HNO₃ and/or NaOH. As it can be seen, the potentials remain constant in the pH range of 2.0 – 5.5 as the working pH range of proposed electrodes. It seems, at higher pH via simultaneous formation of hydroxo complexes or hydroxide precipitate or because of probable change in stoichiometry of metal chelate species a drift in response was achieved. At low pH values by protonation of proposed carrier and various functional group of graphite powder or activated MWCNT, the response performance significantly decreased. Since the pH of Cu²⁺ ion solution over linear range is in this range, this pH ranges was selected as working range without addition of buffer.

3.2. Potentiometric Selectivity

The potentiometric selectivity coefficients of these new electrodes was evaluated by conventional method such as separate solution method (SSM) (at 0.01 M of ions) and fixed interference method (FIM) (0.01 M interfering ions and different concentration of Cu²⁺ ion) and numerical calculated value of selectivity coefficient was calculated and presented in Table 3. As shown in Scheme 1, a tridentate (N₂O) Schiff base has been generated on the MWCNT surface. A hard donor atom (O) and two relative hard atoms (N) are suitable

chelating agents for binding to hard and relatively hard cations. This surface supported Schiff base can be deprotonated via phenolic OH and NH groups and act as two basic chelating agents. Many reports have been done on complexation of copper (II) ion with Schiff bases containing N₂, N₂O₂, N₄, N₂S and etc [82-84]. Therefore, it is expected that the copper ion as relative hard cation reacts with this chelating agent in 1:1 and or 1:2 ratios. Other hard cations maybe inferred with Cu²⁺ based on the extent of their hardness as shown in table 3.

This phenomena, efficiently shows that Cu²⁺ ion interact via a specific type of interaction and carriers structure play a considerable role on the response of the electrodes.

3.3. Dynamic response time

It is well known that the dynamic response time of a sensor is one of the most important factors in its evaluation. This property was examined as required time to achieve equilibrium response over the different concentration in the range of 1.0×10^{-8} to 1.0×10^{-1} mol L⁻¹ and typical curve is presented in Fig. 6. The electrode based on Ag-NP-AC has fast and repeatable response mechanism at about 10 s and is stable for at least 10 min. The similar response time in opposite direction show the reversibility and usability of proposed electrodes in different real samples with various content of analytes. The electrode simply is applicable for Cu²⁺ ion content evaluation by simple re-newing the electrode surface on paper to remove residual adsorbed copper content on the surface of carbon paste electrode. The standard deviation of slope of similar electrodes at optimum conditions specified above (N=6) was between 1.42-1.65. The simultaneous re-calibration of the same electrode at optimum conditions shows not significant change in linear range with standard deviation of slope between 1.74-1.89. The overall characteristic performance of all proposed electrodes is presented in Table 4.

3.5. Determination of Cu^{2+} ion in real samples

The proposed electrodes were applied successfully for Cu^{2+} ion content evaluation in *Cinnamomum zeylanicum* and *Zingiber officinal* that was treated according to experimental section. In these real samples, the analyte content in spike samples was evaluated by standard addition method and respective results are presented in Table 5. As it was observed, the low RSD and high recovery of proposed method indicate its applicability for Cu^{2+} ion determination in various real samples. The proposed electrode was also successfully applied as an indicator electrode in conjunction with a Ag/AgCl reference electrode for the potentiometric solutions with Cu^{2+} ion.

4. Conclusions

A new Cu^{2+} ion selective electrode by impregnation of chemically modified MWCNT in the graphite powder was constructed that is superior to other previously reported Cu^{2+} ion selective electrode in term of wider working concentration range and shorter response time (1.0×10^{-7} to $1.0 \times 10^{-1} \text{ mol L}^{-1}$) with low response time (15 s). This sensor shows good selectivity, high sensitivity and is better than some reported Cu^{2+} selective sensors. The proposed sensor is better when compared to the reported sensors in terms of working concentration range and response time. This chemically modified carbon paste electrode (CMCPE) preparation using this new ionophore is very simple and fast undoubtedly represents one of the most convenient materials for the preparation of modified Cu^{2+} ion carbon paste electrode. As the proposed sensor show high sensitivity wider working concentration range and good selectivity it could be used for the determination of Cu^{2+} in various samples (*Cinnamomum zeylanicum* and *Zingiber officinale*) and is therefore a good addition to the family of Cu^{2+} selective sensors.

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Table1. General Performance characteristics of some copper ion sensors based on various organic ionophores

Ionophore	L..R. ^a	Slope ^b ,	D. L. (μM)	I ^c	pH	R.T ^d	Reference
Thiacrown ethers	10-0.1	22.3	0.14	Pb ²⁺	-----	-----	[48]
ACCP	10- 0.2	29.4	8.0	-----	-----	-----	[49]
-----	7.94- 0.1	29.9 \pm 0.2	-----	Na ⁺ , Co ²⁺	2.1_6.3	11	[50]
-----	10-0.1	Nernstian	-----	-----	1.9 -5.2	<30	[51]
porphyrin	4.4-0.1	29.3	0.28	Ni ²⁺	2.8 -7.9	~8	[52]
TDS	----	31	0.4	K ⁺ , Zn ²⁺ , Pb ²⁺	-----	-----	[53]
NDHA	0.3 - 0.01	30.0 \pm 0.5	0.25	-----	3.0-7.4	<10	[54]
SFP	0.23 - 0.001	29.4 \pm 0.5	0.027	-----	2.3-5.4	8	[55]
Dithiocarbamate	1.0-0.1	28-29	0.4	-----	-----	-----	[56]
TDTSA	0.025-0.0006	68.7	0.013-0.5	Pb ²⁺ , Mg ²⁺ , Cd ²⁺ , Ca ²⁺ , Al ³⁺ ,	-----	-----	[18]
PTD	0.97-0.076	30 \pm 2	0.77	NR	-----	-----	[57]
MD	32-0.1	30	12	Sr ²⁺ , Cs ⁺ , K ⁺ , Na ⁺ , Sr ²⁺	-----	----	[58]
-----	8-0.1	29.5	1.0	Pb ²⁺ , Al ³⁺	-----	-----	[17]
----	1-0.01	30.0	>0.1	-----	----	-----	[59]
Calixazacrown ethers	0.031-0.0031	27.2	10.0	Rb ⁺	-----	-----	[60]
CTP	1-0.01	30.3	0.75	Zn ²⁺ , Pb ²⁺	4.5-7	15 and 20	[42]
ACA	0.22-0.01	29.2 \pm 0.2	0.11	Ag ⁺	4.0-9	15	[32]
BHAB	0.05-0.01	29.6 \pm 0.2	0.04	-----	2.8-5.8	15	[61]
-----	5.0-0.1	29.88	2.34	-----	2.8-7.5	10	[62]
BAPE	10-0.1	30.0	0.5	----	3.3-7.0	10	[63]

a) Linear range (μM -M);b) (mV per decade concentration), c) Intefrence; d) response time (s);Abbreviations: ACCP, Aza-thio ether crowns containing 1,10 phenanthroline;BHAB,Bis(2-hydroxyacetophenone)butane-2,3-dihydrazone;HIPM,Hydrotris(3isopropylpyrazolyl)methan; BAPE,bis(acetylacetone)propylenediimine, PPTD, 3-(2-pyridinyl)-2H-pyrido[1,2,-a]-1,3,5-triazine-2,4(3H)-dithione; EBCC, Ethambutol-copper (II) complex; TDS, Thiuram disulphides; NDHA, N,N'-(2,2-dimethylpropane-1,3-diyl)-bis(dihydroxyacetophenone); SFP, salicylidine-functionalized polysiloxane; TDTSA, Thio and dithiosalicylic acids; PTD, Pyrimidine thione derivatives; MD, Macrocyclic diamides; CTP, cyclic tetrapeptide; ACA, acetoacetanilide;

Table. 2 Response performance of the copper carbon paste electrodes at different compositions based on (CMMWCNT).

N	Carbon powder (mg)	Carrier (mg)	NaTPB (mg)	Nujol (mg)	Ag-NP (mg)	L. R. ($\mu\text{M-M}$)	Slope (mV/decade)
1	50	10	2.0	18	0	0.1-0.01	3.09
2	50	30	2.0	18	0	1.0-0.01	6.09
3	50	60	3.0	18	0	50.0-0.01	18.33
4	50	80	6.0	18	0	0.5-0.01	14.54
5	50	100	2.0	18	0	1.0-0.05	17.24
6	50	120	6.0	18	0	50.0-0.01	46.45
7	50	100	4.0	18	0	5.0-0.1	29.27
8	50	100	6.0	18	0	1.0-0.1	30.84
9	50	100	8.0	18	0	1.0-0.1	38.14
10	50	100	6.0	36	0	1.0-0.1	29.93
11	50	100	0.0	36	0	5.0-0.1	13.08
12	50	100	6.0	36	3.0	0.5-0.005	24.27
13	50	100	6.0	36	5.0	0.1-0.1	29.11
14	50	100	6.0	36	7.0	5.0-0.01	29.98
15	50	100	6.0	36	8.0	10.0-0.1	29.21
16	50	100	6.0	36	10	0.5-0.01	32.01

Table. 3 Selectivity coefficients of the Cu^{2+} ion carbon paste electrodes by separate solution method (SSM) (at 0.01 M of ions) and fixed interference method (FIM) (0.01 M interfering ions and different concentration of Cu^{2+} ion)

Ion	-LogK			
	CMMWCNT		Ag	
	FIM	SSM	FIM	SSM
Na^+	1.45	1.35	1.69	1.88
Zn^{2+}	3.25	2.75	2.81	2.49
Ni^{2+}	3.17	2.67	2.86	2.69
Pb^{2+}	1.18	1.21	2.42	1.36
Cd^{2+}	3.27	2.73	2.76	1.33
Fe^{3+}	1.17	0.96	1.45	1.03
K^+	1.41	1.62	1.54	2.63
Ca^{2+}	2.25	2.72	3.11	2.54
Co^{2+}	2.41	1.87	3.28	3.14

Table. 4 Specification of proposed electrodes based on (CMMWCNT)

Properties	Values / Range	
	(CMMWCNT)	
Electrode type	Carbon paste electrode	
Optimized carbon pasted composition (% by weight)	Carbon powder, CMMWCNT, Nujol, NaTPB (mg) (50 mg: 100 mg, 36 mg, 6 mg)	Carbon powder, CMMWCNT, Nujol, NaTPB, Ag (mg) (50 mg: 100 mg, 36 mg, 6 mg, 5 mg)
pH range	2.0 – 5.0	2.0 -5.5
Linear range	5.0×10^{-6} - 1.0×10^{-1}	5.0×10^{-7} - 1.0×10^{-1}
Slope	29.93	29.11
SD^a	1.52	1.29
Response time (s)	< 15	≈10

a) Standard deviation of slope (within electrode variation, mV/decade)

Table. 5 Application of the proposed electrodes for the determination of copper ion in water samples.

Sample	Added	CMMWCNT		CMMWCNT-Ag	
		Found	Recovery ^a	Found	Recovery ^a
Cinnamomum zeylanicum	0	21.8±0.6	----	21.5±0.4	---
	50	72.4±0.7	101.2	72.0±0.9	101.0
ZINGIBER OFFICINALE	0	26.6±0.7	---	26.2±0.5	---
	50	77.2±0.4	101.2	76.4±0.6	100.4

Figures Caption:

Figure. 1. Schematic diagram of synthesis of chemically modified MWCNT

Figure. 2. FT-IR of activated MWNCT (a), MWCNT- TMSPEDA(b) and MWCNT-SPEDIMP as CMMWCNT (c).

Figure. 3. SEM of chemically modified MWCNT

Figure. 4. BET of chemically modified MWCNT

Figure. 5. Effect of pH of the test solution of Cu^{2+} on the potential response of the Cu^{2+} ion-selective electrode (a): 10^{-1}M , (b): 10^{-2}M . (A): CMMWCNT, (B): CMMWCNT and Ag particles

Figure. 6 Response time of proposed of the Cu^{2+} ion selective electrode based on (A): CMMWCNT, (B): CMMWCNT and Ag particles over the different concentration in the range of 1.0×10^{-8} to $1.0 \times 10^{-1} \text{ mol L}^{-1}$

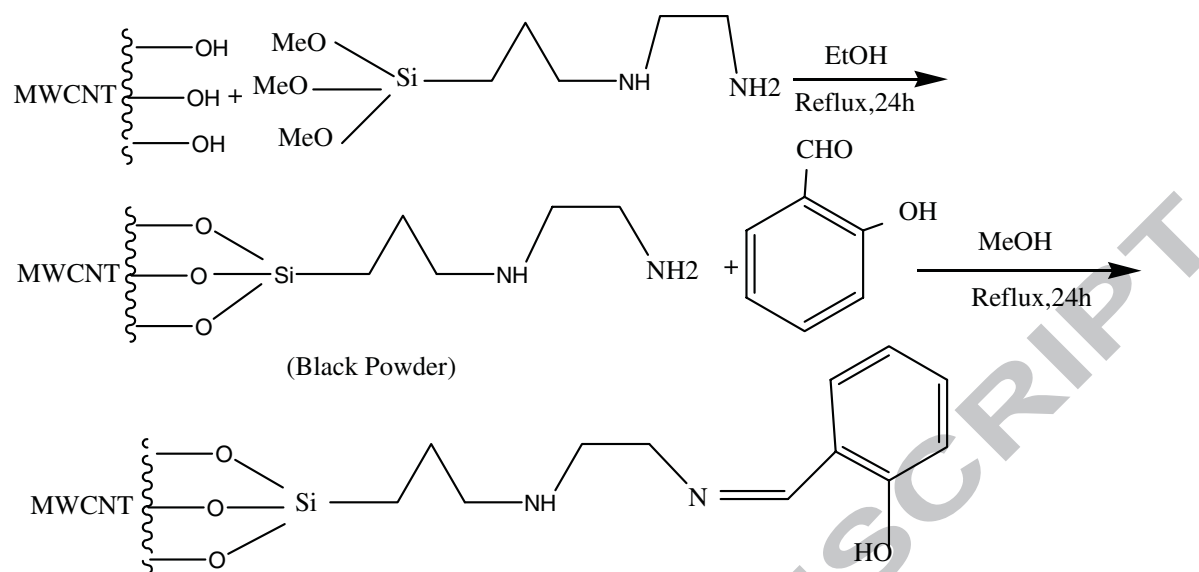


Figure 1

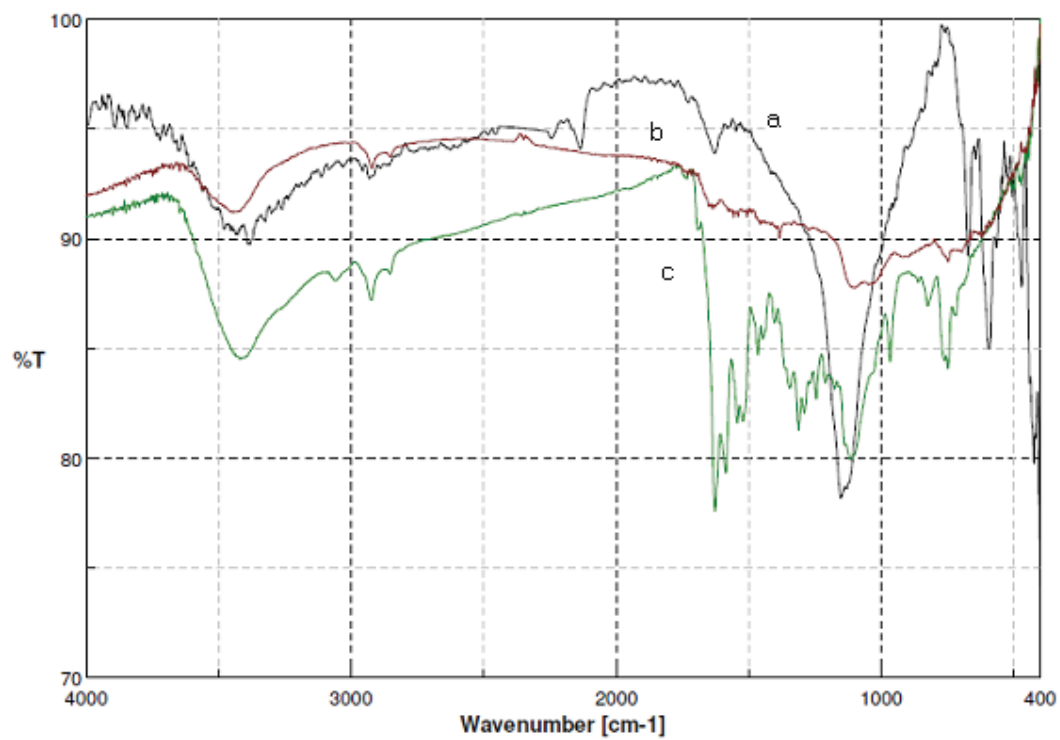


Figure 2

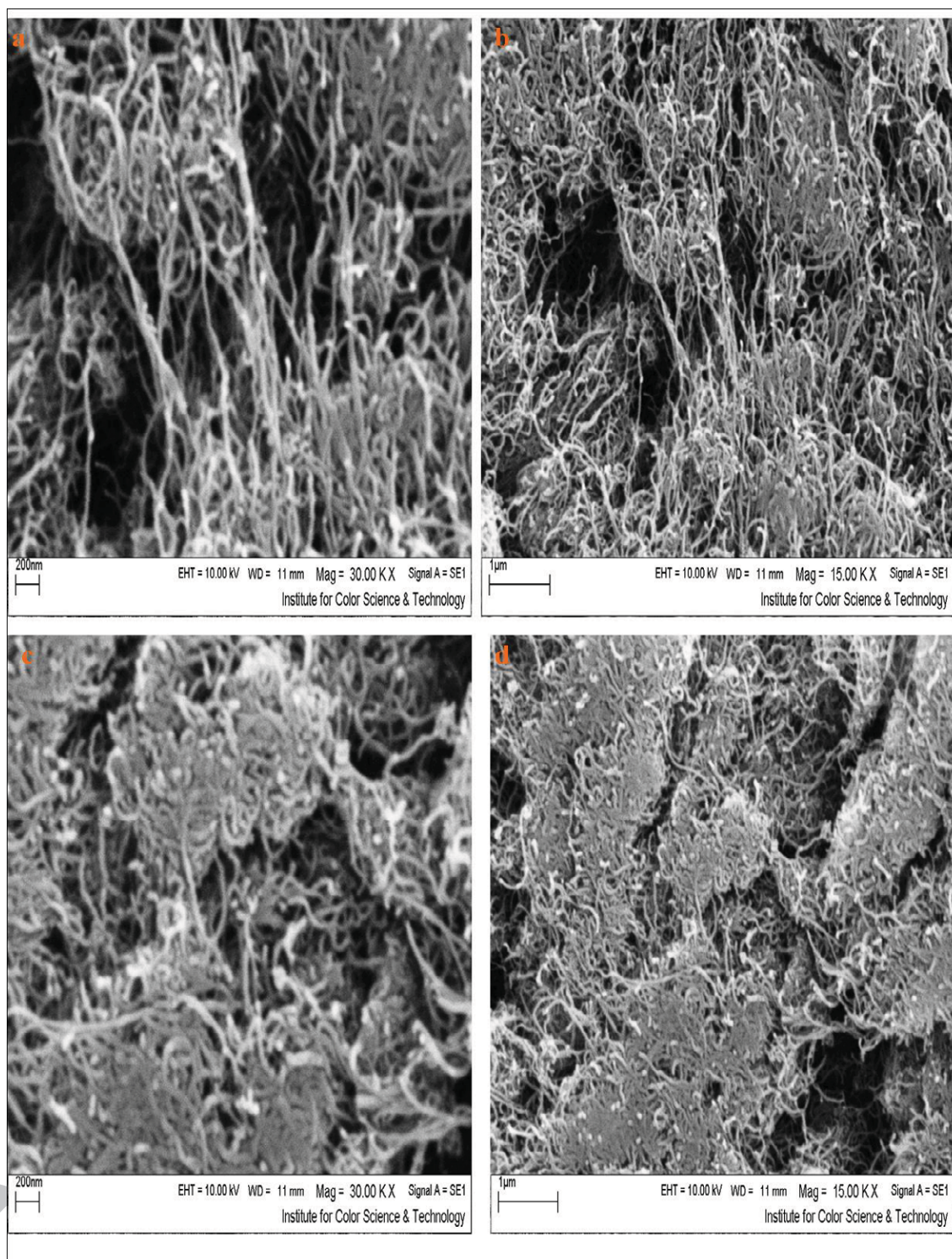


Figure 3

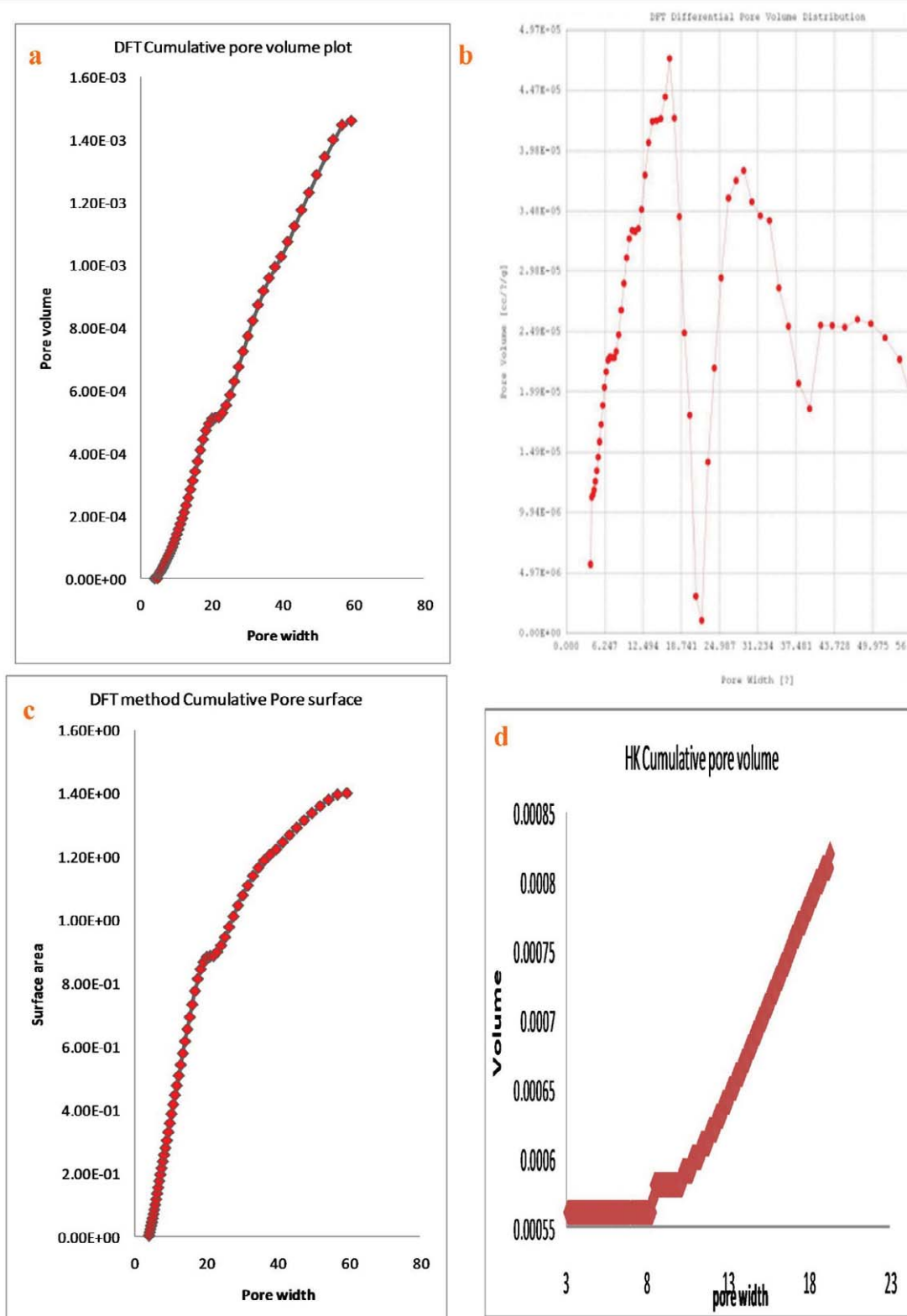


Figure 4

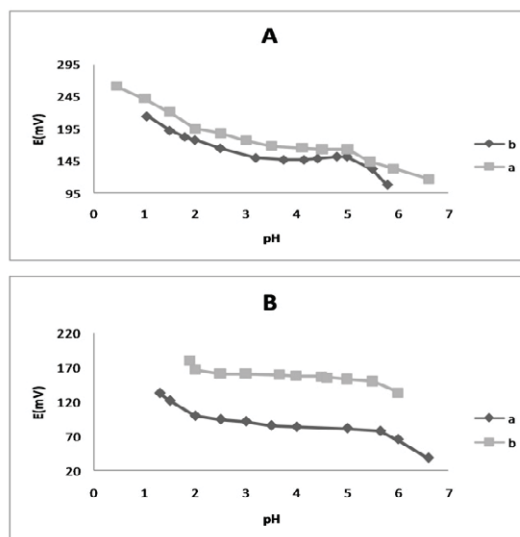


Figure 5

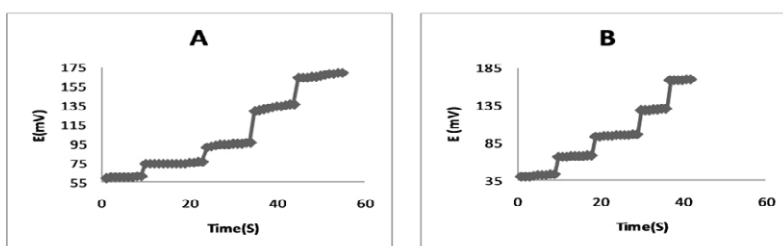


Figure. 6

Chemically modified multiwalled carbon nanotube carbon paste electrode for copper determination

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