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Synthesis and Application of MWCNT-SPIMP as a Suitable Neutral Carrier for Construction of New Copper Selective Carbon Paste Electrode

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In this research Multi-walled carbon nanotube (MWCNT) surface was modified chemically by a couple of reactions between trimethoxysilyl- propyl-amine (TMSPA) and (2)-hydroxybenzaldehyde (2-HBA) which is then characterized by FT-IR technique. This new material (MWCNT-SPIMP) in carbon paste electrode, matrices selectively the Cu^{2+} ion. The influence of variables including sodium tetraphenylborate ($(C_6H_5)_4BNa$), some amount of MWCNT-TMSPA, Nujol and graphite powder on electrode response has been investigated and their value was set as graphite powder: NaTPB: Nujol: carrier in the mass (mg) ratio of 150/6.0/30.0/50 for this electrode. At the optimum it was set as the proposed ion selective electrode response, and is linear over the wide range concentration of 1.0×10^{-8} to 1.0×10^{-2} mol L^{-1} with slopes of 30.01 per decade of ion concentration and detection limit of 8.8×10^{-9} mol L^{-1}. The response of this electrode is independent of pH in the range of 3.0-6.0 with a short response time of about 5s. This electrode successfully has been applied for potentiometric determination of Cu^{2+} ion content in various real samples and as indicator electrodes for potentiometric titration.

Keywords: Cu^{2+}-selective electrode, Potentiometric sensor, Carbon paste electrode, Multiwalled Carbon Nanotubes.

1. INTRODUCTION

Copper is one of the heavy metals and determination of this ion in environmental and industrial samples is very important. A low concentration of copper is essential for living but in high concentration it is very toxic [1]. Therefore, the copper content in many samples must be controlled and determined with low-cost, simple, rapid, remote, and on-line methods [2–8]. Atomic absorption spectrometry (AAS) [9, 10], cold vapor AAS or flame AAS with electro-hermal atomization [11, 12], inductively coupled plasma emission spectrometry [13, 14], gravimetry [15, 16], chromatography [17], and anodic stripping voltammetry [18, 19]. Most of the this methods usually have low detection limit and high selectivity, but also in many cases it possess drawbacks such as high cost of equipment, expensive materials, time-consuming procedures and complicated operations. At the same time, ion-selective electrode (ISE) is a fast method for determination of various ions. This method has advantages such as simple instrumentation, relatively fast response, wide concentration range, reasonable selectivity and low cost of materials. The important component of ISE composition is the complexing agent (carrier, ionophore) that shows selective response to one ion in the presence of interfering ions.

Carbon pastes are useful materials for construction of various electrometric sensors for analytical purposes [20–22].

The carbon paste electrode can be chemically modified (CMCPE) with suitable materials and agent to show selective response to target species.

In comparison with ion-selective electrodes based on polymeric membranes, the CMCPEs possess advantages of much lower ohmic resistance, has a very stable response and easy renewal of its surface. However CMCPEs have been mainly applied in voltammetric analysis [23, 24] and only few of these electrodes have been used in potentiometry.

Nanotechnology is nowadays one of the most important trends in science, perceived as one of the key technologies of the present century. In recent years, carbon nanotubes (CNTs), a novel member in the carbon family, have attracted great attention due to its advantages that can be used for many different applications in terms of its chemical, electronic and mechanical properties as well as the unique tubular structures and large length/diameter ratio. CNTs are to be considered as a sheet of graphite that has been rolled into a tube and are classified as single–walled carbon nanotubes (SWCNTs) and also multi-walled carbon nanotubes (MWCNTs). Now over the past 20 years, CNTs have been exploited in analytical and other fields such as biosensors with immobilized biomolecules, electrochemical detectors, gas sensor, catalyst supports and so on [25-32].

Due to low selectivity and efficiency of untreated or oxidized-Multiwalled carbon nanotubes (MWCNT), modification of its surface with various functional groups makes it a suitable and selective material for various ion determination [33-37] So, it is expected that MWCNTs modified with organic compounds would be more selective than untreated and oxidized-MWCNTs for the complexation of metal ions. In this research the surface of MWCNTs was chemically modified by a couple of reactions between TMSPA and 2-HBA, and this new material (MWCNT-SPIMP) was used for fabrication of carbon paste electrode for selective determination of Cu^{2+} ion. This prepared electrode has good properties such as wide concentration range (1.0×10^{-8} to 1.0×10^{-2} M), good Nernstian slope, long life time and fast response time. The electrode can be used successfully for determination of Cu^{2+} ion in real samples.

2. EXPERIMENTAL

2.1. Apparatus, Reagents, and Materials

For pH and potential measurements a pH/Ion meters model 691 Met Rohm (Switzerland) was applied. All chemicals with the purity of analytical reagent grade and doubly distilled water were used throughout. Pure Graphite powder and Nujol oil that were used in metrics of carbon paste were purchased from Fluka (Buchs, Switzerland) and high pure MWCNT was purchased from Merck (Darmstadt, Germany). The stock solution of copper ion was prepared by dissolving appropriate amount of its nitrate in doubly distilled water. MWCNT-SPIMP that was used as ionophore in carbon paste was synthesized in our laboratory according to our previous publications (Fig. 1) [28, 38]. For SEM studies of materials the scanning electron microscope Leica/Cambridge S360 was used

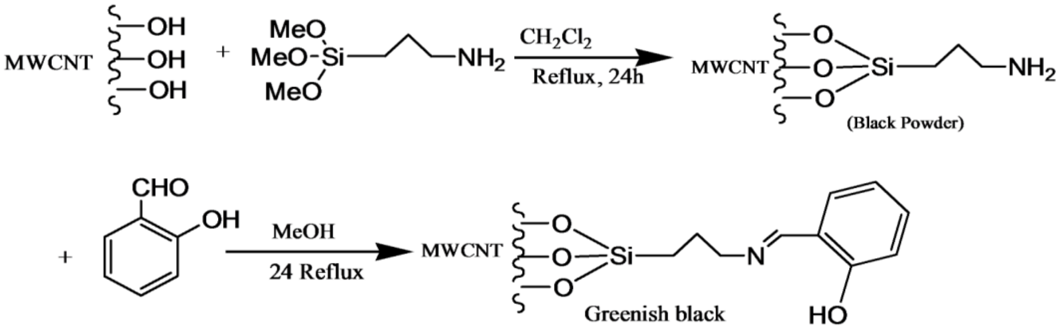

Figure 1. Schematic diagram of the synthesis of proposed ionophore.

2.2. Electrode Preparation and Potential Measurements

Unmodified carbon paste was prepared by hand mixing of 150 mg of reagent-grade graphite powder and 25 mg of Nujol oil in mortar with a pestle. Modified carbon paste with various compositions was prepared by mixing 150 mg of carbon with different weight of Nujol, ionophore and additive to get different compositions as given in Table 2. Prepared carbon pastes were packed into a polyethylene syringes with 5.0 mL volume and 2.5 mm diameter and a thin copper wire was glued on the end of carbon paste for electrical contact.

2.3. Electromotive Force (EMF) Measurements

The EMF measurements were carried out with the following cell assemblies: CPE| Sample solution| double junction Ag/AgCl reference electrode, with a pH/mV meter. A conventional glass pH electrode was used for monitoring of pH of the sample solutions simultaneously. For investigation of performance of each electrode, the electrode and reference electrode were putted into vial of Cu^{2+} solution that was stirred, then the recorded potential were plotted versus the logarithm of Cu^{2+} ion concentration in the range of 1.0×10^{-8}–1.0×10^{-2} $mol.L^{-1}$ by serial dilution of the 0.5 $mol.L^{-1}$ stock solutions at constant ph. In real samples the accuracy was examined by standard addition method.

3. RESULT AND DISCUSSION

The MWCNT-SPIMP was synthesized according to Fig. 1 [28, 38], and characterized by FT-IR analysis (Fig. 2) and then the surface properties such as size and homogeneity of this material studied by SEM (Fig. 3) [28, 38]. In Fig. 2 the high frequency region, broadened bands around 3461 cm^{-1} can be observed in two cases, which can be assigned to the bending vibrations of adsorbed molecular water and stretching vibrations of OH groups. The band observed at about 1128 cm^{-1} could be assigned to the C–O group in MWCNTs. The spectra (Fig. 2-B) display a number of absorption peaks, indicating the trimethoxysilyl-propyl-amine. The absorption around at 1018 cm^{-1} corresponds to Si–O stretching vibration. The FT-IR spectroscopic analysis indicated broad band at 3326 cm^{-1}, representing bonded –NH$_2$ groups. The band observed at about 2886 cm^{-1} could be assigned to the aliphatic C–H group. The spectrum of MWCNTs-.Schiff base (Fig. 2-C) the bands appeared at 1665 cm^{-1} due to imine (mainly ascribed to the C=N stretching band). These bands are due to the lattice hydroxyl and aromatic groups, in the range 1400 – 750 cm^{-1}. Fig. 3 shows that the proposed material has a homogeneous surface morphology with various pore sizes. In previous publications, the MWCNT-SPIMP was optimized and applied for preparation of Zn^{2+} and Al^{3+} CPEs [28, 38]. Therefore, in this research it was optimized for fabrication of Cu^{2+} selective electrode with different carbon paste composition.

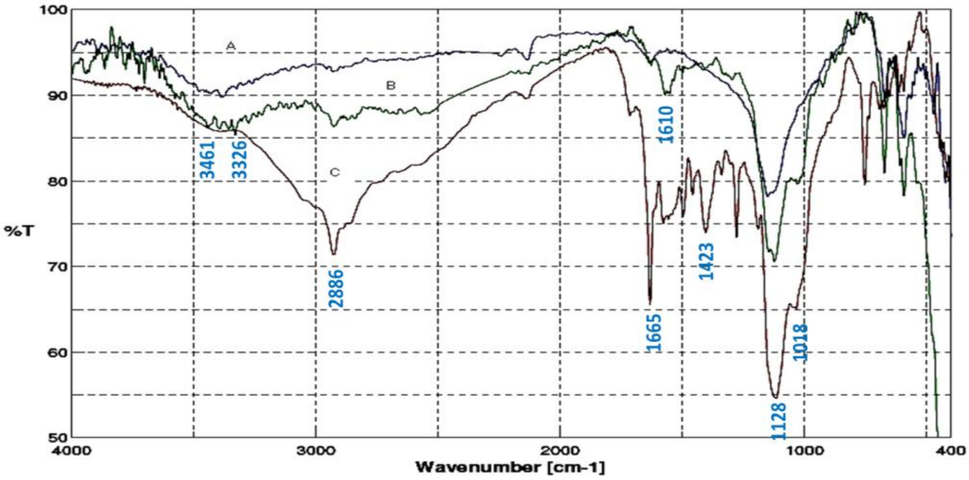

Figure 2. FT-IR spectra of (A) Multiwalled carbon nanotube, (B) surface supported by trimethoxysilyl-propyl-amine, (C) modified Multiwalled carbon nanotube (MWCNT-SPIMP)

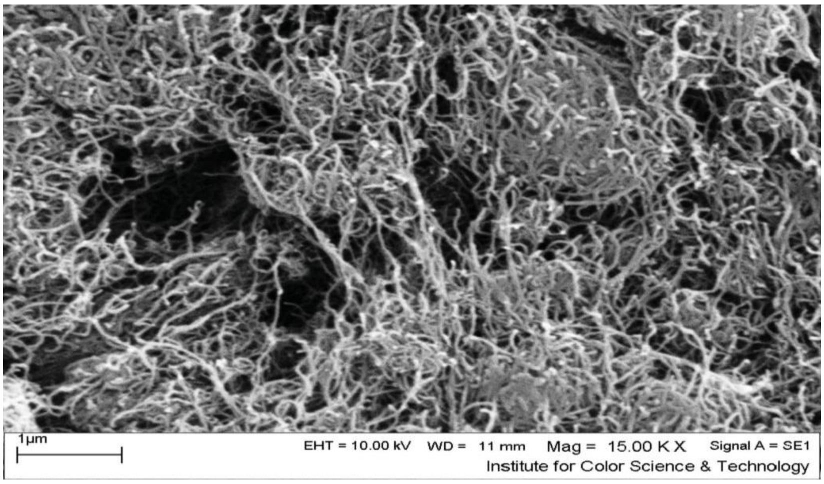

Figure 3. SEM micrographs of MWCNT_SPIMP.

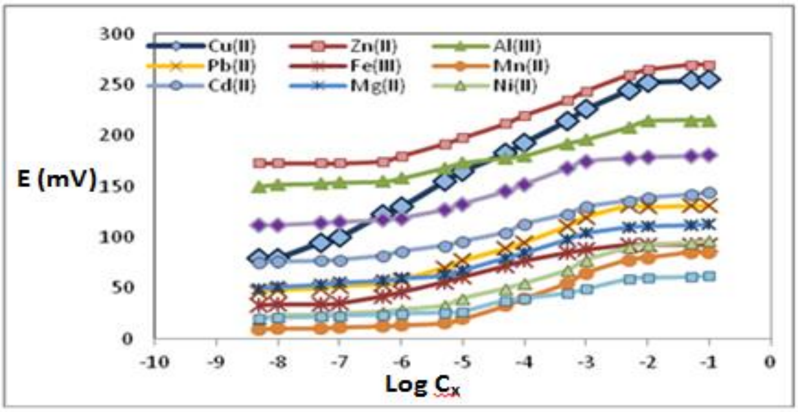

Figure 4. Potential response of prepared electrode for various ions.

Potential response of prepared electrode for various metal ions figure shows that among them the response toward Cu^{2+} ion is near Nernstian in a wide concentration range (1.0×10^{-8} to 1.0×10^{-1}mol L^{-1}) (Fig. 4).

3.1. Influence of carrier composition (2-HBA and TMSPA) and electrode composition on the electrode Response

To improve the response of this new Cu^{2+} selective electrode, carrier composition (2-HBA and TMSPA) and electrode composition was optimized. The results are presented in Tables 1 and 2.

Table 1. Influence of ionophore (MWCNT-SPIMP) composition on the response of electrode.

No	MWCNT (mg)	2-HBA (mg)	TMSPA (mg)	Linear range (μM-M)	Detection Limit (μM)	Slope (mV/decade)	Response time (S)
1	100	3.3	6.6	0.1-0.005	0.09	20.1	15
2	**100**	**2.2**	**4.4**	**0.05-0.01**	**0.04**	**25.7**	**10**
3	100	1.1	2.2	0.1-0.01	0.08	21.3	12

According to *figure 1* the carrier is prepared from reaction of TMSPA and 2-HBA on the surface of MWCNT, so the amount and ratio of both species must be optimized. As it can be seen in Table 1, using carrier composed of 2.2 g 2-HBA and 4.4 g of TMSPA lead to obtain Nernstian response with wide concentration range, so this ratio was selected for synthesis of carrier.

Table 2 shows that the blank carbon paste (carbon, additives and Nujol) show a poor response to Cu^{2+} ion (non-Nernstian slope 43.0 per decade^{-1} and a short linear range1.0×10^{-5} to 5.0×10^{-3}mol L^{-1}). The response was significantly improved by addition of carriers. Amount of carrier to improve the electrode response was optimized. As it was shown in table 2, 50 mg of carrier is sufficient to improve the performance of this electrode. Further additions of carrier significantly diminish the response, probably due to the saturation of the electrodes or un-homogeneity in the electrode surface.

Generally, electrode composition effects on behavior and selectivity of the electrode. Addition of lipophilic additives with negative charge increases the extraction capability of the carriers and reduces the ohmic resistance of CMCPE and improves selectivity and response of cation-selective electrode [39].

Table 2. Influence of electrode composition on the response of electrode

No	Graphite (mg)	MWCNT-SPIMP (mg)	DMS (mg)	Nujol (mg)	DBP (mg)	Additive (mg)	Linear range (μM-M)	Detection Limit (μM)	Slope (mV/decade)
1	150	40	-	25		5	0.05-0.01	0.04	24.1
2	150	50	-	25	-	5	0.01-0.01	0.01	25.5
3	150	60	-	25	-	5	0.05-0.01	0.05	25.0
4	150	75	-	25	-	5	0.1-0.005	0.09	24.0
5	150	100	-	25	-	5	0.5-0.001	0.50	23.8
6	150	50	-	25	-	0	0.1-0.005	0.08	21.3
7	150	50	-	25	-	2	0.05-0.01	0.03	24.1
8	150	50	-	25	-	4	0.01-0.01	0.009	26.5
9	150	50	-	25	-	6	0.01-0.01-	0.008	30.8
10	150	50	-	25	-	8	0.01-0.01	0.01	28.0
11	150	50	-	25	-	10	0.05-0.005	0.03	24.3
12	150	50	25	-	-	6	0.05-0.01	0.05	33.6
13	150	50	-	25	-	6	0.01-0.01	0.008	30.6
14	150	50	-	-	25	6	0.01-0.01	0.01	32.5
15	150	50	-	20	-	6	0.01-0.01	0.009	33.3
16	**150**	**50**	**-**	**30**	**-**	**6**	**0.01-0.01**	**0.008**	**30.01**
17	150	50	---	40	---	6	0.01-0.01	0.008	27.4
18	150	50	---	50	---	6	0.05-0.005	0.04	24.1
19	150	0	-	30	-	6	10.0-0.005-	9.50	43.0

Tables 2 shows that without the additive the electrode has a low linear response and a high detection limit (with a slope of 21.3 per decade^{-1}). Addition of 6 mg NaTPB improves the sensitivity and linear range of electrode.

The pasting liquid needs to be chemically inert to form a paste mixture with fine consistency. In this work, influence of kind and amount of plasticizers were investigated and found that a stable and reproducible potentiometric response was achieved using 30 mg Nujol oil. The slop of 30.01 per decade^{-1}and the linear range 1.0×10^{-8} to 1.0×10^{-2} mol.L^{-1} was obtained for the electrode. The detection limits was 8.8×10^{-9} mol.L^{-1}.

3.2. Effect of pH of the Test Solution

The potentiometric response of proposed electrode significantly depends on pH. Therefore, the effect of pH over the pH range of 1.0–8.0 at two Cu^{2+} ion concentrations of 1.0×10^{-3} and 1.0×10^{-2} mol L^{-1} was examined and results is shown in Fig. 5.

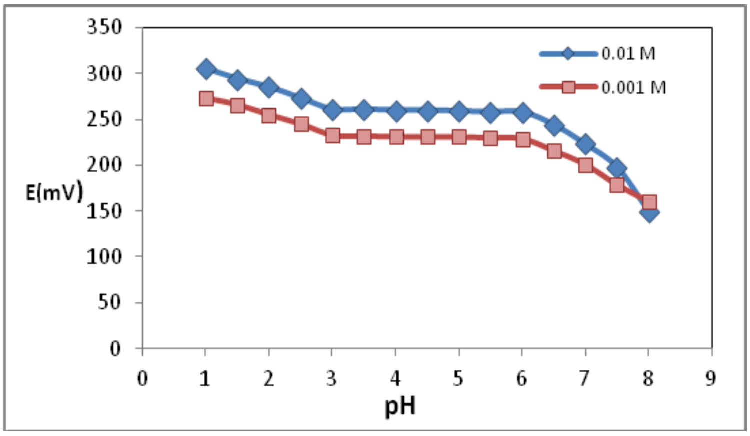

Figure 5. Effect of pH of solution on the electrode response in presence of 1.0 × 10^{-2} and 1.0 × 10^{-3} mol L^{-1} Cu^{2+} ion solutions.

Figure 5 shows that the electrode response was independent on pH in the range of 3.0–6.0 that this range was taken as the working pH range of the electrode. At low pH value, the electrode response was affected by chelating sites such as nitrogen atom and hydroxyl group of MWCNT-SPIMP. At higher pH, because of formation of some hydroxyl complexes of Cu^{2+} ion, the electrode response was affected.

3.3. Selectivity Sequence of Proposed Cu^{2+} Ion Selective Electrode

Table 3. Selectivity coefficients of the proposed electrode

Ion	-Log K		
	SSM	FIM	MPM
Pb^{2+}	2.55	3.07	2.86
Ni^{2+}	3.18	2.66	2.92
Cd^{2+}	3.31	3.08	3.12
Co^{2+}	2.15	2.33	2.26
Al^{3+}	0.95	0.86	0.91
Zn^{2+}	0.91	0.94	0.85
Fe^{3+}	0.88	0.82	0.95
Hg^{2+}	3.37	3.04	3.55
Ag^{+}	3.81	3.54	3.12
Cr^{3+}	2.55	2.42	2.61
Mn^{2+}	2.76	2.43	2.56
Ca^{2+}	3.12	3.00	3.25
Na^{+}	3.48	3.15	3.36
K^{+}	3.49	3.27	3.11
Ba^{2+}	3.06	3.18	3.10
Mg^{2+}	3.14	3.25	3.02

The effect of interfering ions on the measuring potential of a membrane sensor has been described in terms of selectivity coefficient. The selectivity coefficients can be measured by various methods namely separate solution method (SSM) [35]. Fixed interference method (FIM) [36] and matched potential method (MPM) [37]. In this work three methods were used for determination of electrode signal in the presence of interfering ions. In FIM the potential of proposed sensor to various amount of Cu^{2+}ion (1.0×10^{-2} to 1.0×10^{-8} M) in the presence of fixed concentration of interfering ion (1×10^{-2} M) was recorded. According to MPM, the selectivity coefficient is defined as the activity ratio of the primary ion and the interfering ions that gives the same potential change in a reference solution and measure the change in potential upon changing the primary ion activity. The obtained results and calculated selectivity coefficients for common inorganic and organic interfering ions shown in Table 3. It is obvious from the obtained values that the Cu^{2+}ions sensor shows high selectivity towards Cu^{2+}ions over other ions.

3.4. Response time

One of the critical limiting factors in the application of ion selective electrodes is response time. The response time is defined as time required for the electrodes to reach 90% of its equilibrium potential, after successive immersions in a series of solutions with 10-fold concentration difference [40–43]. The response time of proposed sensor evaluated by measuring the required time for achieve the steady state potential over the concentration range of 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1}. As can be seen in Fig 6, the fabricated electrode was fast (<5 s) which is very short response time in comparison with some previous researches [44].

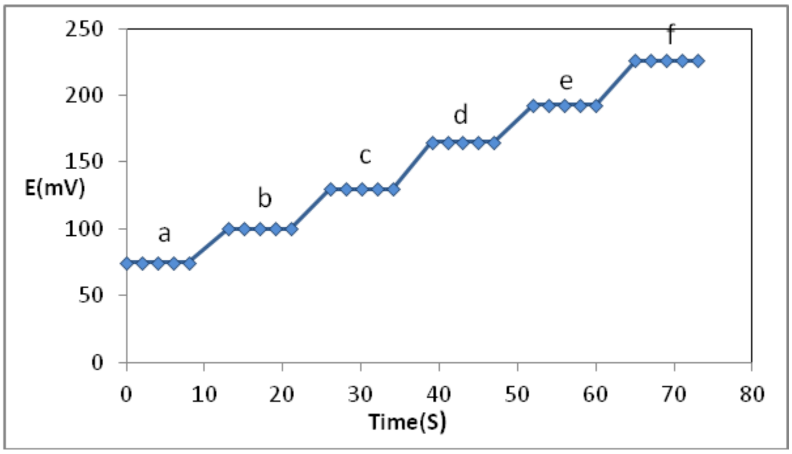

Figure 6. Response time of proposed electrode in different concentrations of Cu^{2+} solutions. (a) 1.0×10^{-7}, (b) 1.0×10^{-6}, (c) 1.0×10^{-5}, (d) 1.0×10^{-4}, (e) 1.0×10^{-3}, (f) 1.0×10^{-2} mol.L^{-1}

3.5. Analytical Applications

The proposed electrode was successfully applied for the potentiometric titration of Cu^{2+} ion solution with EDTA solution at pH 5.0 (Fig. 7). The good and accurate equivalent point shows the good performance of this electrode for determination of Cu^{2+} ion. The proposed electrode was applied for determination of Cu^{2+} ion in tea leaves and various water samples as an indicator electrode. The copper content in tea sample was extracted as described in ref. [45]. Results were found to be in satisfactory agreement with that determined by atomic absorption spectrometry (AAS) (Table 4). As Table 4 shows, it can be concluded that, the electrode may have applications in the real sample monitoring of Cu^{2+}ions

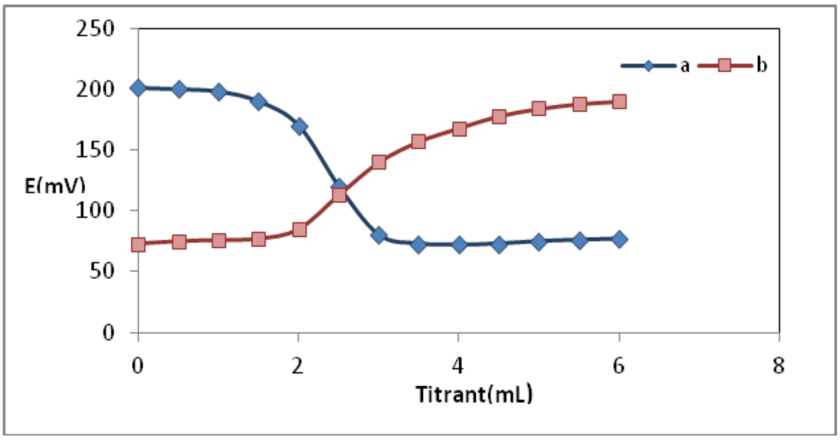

Figure 7. Titration curve of (a) 25 mL of 0.001 mol L^{-1} of Cu^{2+} solution with 0.01 mol L^{-1} of EDTA solution and (b) reverse.

Table 4. Determination of Cu^{2+}in real samples

Sample	Cu^{2+} Found (M)	
	MCPE	AAS
Tea leaves	8.5×10^{-4}	8.2×10^{-4}
Waste water	4.1×10^{-4}	3.8×10^{-4}
Well water	1.0×10^{-4}	1.2×10^{-4}
River water	9.6×10^{-5}	9.3×10^{-5}
Industrial water	1.9×10^{-3}	1.7×10^{-3}
Mineral water	2.2×10^{-4}	2.3×10^{-4}

4. CONCLUSIONS

On the basis of the results discussed in this paper, MWCNT-SPIMP is a suitable carrier for fabrication of a Cu^{2+} selective electrode. The proposed electrode has been shown to have good operation characteristics such as sensitivity, stability, response time, detection limit and a wide linear working range. The electrode was successfully applied for the determination of Cu^{2+} content in aqueous solutions. Table 5 lists linear range, detection limit, response time and slope of some of the Cu^{2+} selective electrodes against proposed Cu^{2+} selective electrode for comparative purposes. In comparison with most commercially available electrodes, this proposed electrode had wide linear rang with a low detection limits and fast response time (Table 5) [44, 46-52].

Table 5. Characteristics performance of some Cu^{2+} Ions sensors Based on various ionophores

Ref.	Carrier	Slope (mV/decade)	Linear rang (µM-M)	Detection limit (µM)	Response time (S)
[44]	2-Quinolyl-2-phenylglyoxal-2-oxime(phenylglyoxal-alphamonoxime)	28.2	1.0-0.1	0.5	10-50
[46]	Schiff base (2,3-diaminopyridine +o-vanillin)	29.6	5.0-0.1	3.0	30
[47]	2-((2-(2-(2-(2-hydroxy-5-methoxybenzylideneamino)phenyl)disufanyl)phenylimino) methyl)-4-methoxyphenol	29.54	0.12-0.1	0.09	9
[48]	*p*-hydroxyacetophenone semicarbazone	29.8	0.18-0.1	0.05	5
[49]	4-Amino-6-methyl-1,2,4-triazin-5-one-3-thione	29.3	1.0-0.1	0.62	20
[50]	1,2,5,6,8,11-Hexaazacyclododeca-7,12-dione-2,4,8,10-tetraene	29.5	0.2-0.1	0.08	5
[51]	MWCNT–SPAEIMP-AG-NP-AC	29.93	0.5-0.1	0.25	< 15
[52]	N,N′-(2,2-dimethylpropane-1,3-diyl)-bis(di-hydroxyacetophenone) (NDHA)	30.05	0.3-0.01	0.25	< 10
Present work	MWCNT-SPIMP	30.01	0.01-0.01	0.008	< 5

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